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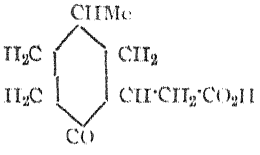
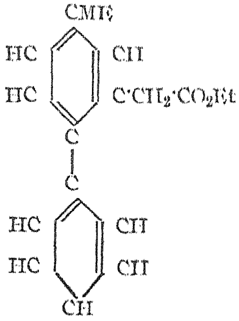
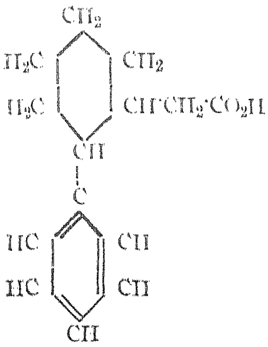
ERRATA

Page.	*Line.*	*Read.*	*For.*
21	8	$\mathrm{R : \overset{:\longrightarrow}{N}\quad : \overset{+}{N} :}$	$\mathrm{R.N \overset{:\longrightarrow}{:}\quad : \quad \overset{+}{N} :}$
44	2	omit "an equiconducting solution."	
46	5	*i.l*	*c.l*
47	22	0·1 milliampere	1 milliampere
	25	*X/Ak*	*X Ak*
48	Table I column 7 last line	80·8	8·08
49	Table II, column 4	$v_{cl'} \times 10^5$	$v_{p'} \times 10^5$
	column 5	$v_{p'} \times 10^5$	$N_{cl'} \times 10^5$
53	Table III	Average 0·591	Average 0·59·1
56	Table VII, column 1 last line	*N*/235-HP	N/277-HP
62	Table XI, column 8	specific condty.	obs. sp. condty.
62	Table XI column 8, lines 3, 4, 5	0·0011	0·0077
63	Line 11	for aqueous solutions;	evaluating for *D*, *T*, etc;
63	1 & 2	agrees fairly well with the value obtained from the measurement of Shedlovsky at 25° and extrapolating to 35° with Kohlrausch's temp. coefficient for Cl'-ion ($v_{cl'}$ at 35° = 92·6 × 10^{-5} cm/sec.)	agrees fairly well with correct value.
202	Fig. 3	......tartrate, PO_4''', etc.	...PO_4''', tartrate, etc.
	Line 7	Tables IV and V.	Tables VI and VII
	Table VI, column 1, last line	2	
376	Fig. 2	*N*/300-$BaCl_2$	*N*/309-$BaCl_2$
384	Eq. (*i*) and (*ii*)	ξ	ζ

Page.	*Line.*	*Read.*	*For.*
385	Eq. (10) as	$v = \frac{N\alpha}{K} + \frac{K\alpha}{1+K\alpha}\int K\alpha$	
386	Eq. (a) and (a')	$4\pi\sigma$	$\pi\sigma$
392	7*	2203	1103
393	1*	quinone part	quino part
	4	quinhydrone	quinohydrone
	12 Table (a)	12·15 c.c.	12·05 c.c.
	14	17·15	17·17
394	8*	sodium acetate	acetic acid
	16	*Add* Vol. at equiv. point = 5·15 c.c.	
424	4*	$[\alpha]_D^{20}$ (c = 1·08 in EtOH	$[\alpha]_D^{20}$
425	3	*Add* (c = 2·57 in $CHCl_3$)	
	6	,, (c = 1·03 in ,,)	
	9	,, (c = 0·5 in ,,)	
451	17*	value	volume
454	Fig. 1	pH 6·5, 7·5, 8·5, 9·5,	5·5, 6·5, etc.
460	Table VI	NH_4 Et_2	NH_4 Et_2
539	7*	$C_{12}H_{18}O_6$	$C_{12}H_8O_6$
,,	6*	(VI)	(II)
541	14	mixed m.p. 148°-49°	mixed m.p.
572	11	1½ hr.	1 hr.
573	25	305°	395°
590	19	(225g.)	(125g.)
,,	25	-1-α-cyanoglutarate	-1-cyanoglutarate
593	Formula (II)		
	,, (IV)	 CMEt HC CH HC C·CH₂·CO₂Et C C HC CH HC CH CH	

* From bottom.

593	,, (V)		
597	17*	$C_{17}H_{18}O_2$	$C_{18}H_{17}O_2$
598	5*	205-15°/7mm.	205-15°/mm.
598	11*	-2-carboxylate-2-acetate	-2-carboxylate
751	8	II	XI
,,	,,	with invariably	invariably
753	13	quantities	qualities
	1*	sulphurous	sulphuric
754	Last column 4th figure	0·004	0·006

* From bottom.

JOURNAL
# of the
INDIAN CHEMICAL SOCIETY

Volume XIII, 1936.

CONTENTS

PAGE

1. Oxidation of Monochloroacetic Acid by Potassium Permanganate at Wave-lengths $366\mu\mu$ and $436\mu\mu$ with Uranyl Salt as Photosensitiser.—By J. C. Ghosh and B. B. Ray 1
2. Action of Dyestuffs and other Substances on Milk Dehydrogenase. Identity of Schardinger Enzyme with Xanthine Oxidase.—By Kali Pada Basu and Sati Prasad Mukherjee 11
3. Electronic Theory of Valency and the Constitution of Aromatic Diazo Compounds.—By Pulin Bihari Sarkar 19
4. Available Nitrogen in Tropical Soils. Part I.—By N. R. Dhar and S. K. Mukherji 23
5. Interaction of Sulphur Dichloride with Substances containing the Reactive Methylene Group. Part II.—By K. G. Naik and S. A. Vaishnav 25
6. Interaction of Thionyl Chloride with Substances containing the Reactive Methylene Group. Part V.—By K. G. Naik and S. A. Vaishnav 28
7. Halogenation. Part XIII. Bromination and Iodination of some Halogenated Benzenes.—By Phuldeo Sahay Varma and S. Shankarnarayanan 31
8. On the Proteinase in the Milky Juice of *Calotropis Gigantea*. Its Purification and Activation by Ascorbic Acid and Glutathione.—By Kali Pada Basu and Madhab Chandra Nath 34
9. A Method for the Estimation of Lead Volumetrically by Fajan's Method.—By Sachindra Nath Roy ... 40

PAGE

10. On the Measurement of Absolute Rates of Migration of Ions by the Method of Moving Boundaries. Part II.—By Jnanendra Nath Mukherjee, Ramprasad Mitra and Narayan Chandra Sen-Gupta 42
11. The Preparation of Thorium Phosphate Gels.—By S. M. Mehta, M. U. Parmar and Mata Prasad ... 69
12. A Modified Micro-method for the Estimation of Nitrogen in Soil.—By Srish Kumar Saha 72
13. Analytical Uses of Nessler's Reagent. A Preliminary Note.—M. Gowsami and B. C. Das-Purkayastha ... 73
14. Behaviour of Gases under the Influence of High Frequency Discharge. Ammonia and Hydrogen.—By B. S. Srikantan 79
15. Formation of Heterocyclic Compounds from Thioacetylcarbamic Acid Derivatives. Part I.—By Tejendra Nath Ghosh 86
16. Dyes derived from Acenaphthenequinone. Part V. 2- (6-Methyl)-thionaphthene-acenaphthylene-indigos.—By Sisir Kumar Guha 94
17. Dyes derived from Acetylene Dicarboxylic Acid.—By Ram Nath Misra and Sikhibhushan Dutt 98
18. The Stereochemistry of Trivalent Nitrogen Compounds. Part I. The Attempted Resolution of some Substituted Derivatives of Aniline.—By E. V. Menon and D. H. Peacock 104
19. Constituents of the Seeds of *Blepharis Edulis*, Pers. Part. I.—By Jagraj Behari Lal 109
20. Active Principles of *Myrsine Africana*, Linn.—By S. Krishna and B. S. Varma 115
21. Constitution of the Reduction Product of Chloral Acetamide. —By (Late) A. N. Meldrum and G. M. Vad ... 117
22. Condensation of Chloral and Bromal with Polyhydric Alcohols.—By (Late) A. N. Meldrum and G. M. Vad 118
23. An *X*-ray Investigation of the Crystals of Benzoin.—By Mata Prasad and Jagdish Shanker 123
24. Viscosity of Thorium Phosphate Gel-forming Mixtures during Gelation.—By S. M. Mehta, M. U. Parmar and Mata Prasad 128
25. Immersion Pyknometer.—By Walter Jung 136

PAGE

28. Complex Compounds of Iridium. Part IV.—By Prafulla Chandra Ray and Nripendra Nath Ghosh... ... 138
27. Studies in the Coagulation of Colloids. Part XI. Coagulation of Optical Refractivity during the Coagulation of Colloid Manganese Dioxide and the New Evidence for the Discontinuity of the Change.—By Shridhar Sarvottam Joshi and S. Jaya Rao 141
28. Application of the Thiocyanogen Value in the Quantitative Determination of Oleic and Linolic Acids in Natural Oils, which are free from Linolenic Acid, according to Kaufmann·—By S. K. Sharma 151
29. New Aspects of Nitrogen Fixation and Conservation in Soil. Part I.—By N. R. Dhar and S. K. Mukerji ... 155
30. Oxidation of Nitrites to Nitrates in Sunlight.—By N. R. Dhar and S. P. Tandon 180
31. Condensation of Chloral with Acid Amides. Properties of -CH(OH)·CCl_3 Group.—By (Late) Andrew Norman Meldrum and Moreshwar Govind Bhojraj 185
32. Halogenation. Part XIV. Iodination of Aromatic Hydrocarbons and Bromotoluenes.—By Phuldeo Sahay Varma and C. Sreenivasmurthyachar 187
33. Halogenation. Part XV. Chlorination and Bromination of Cumene and *p*-Cymene.—By Phuldeo Sahay Varma and M. K. Srinivasan 189
34. Halogenation. Part XVI. Bromination and Iodination of Mesitylene.—By Phuldeo Sahay Varma and T. S. Subrahmanian 192
35. Parachor and Chemical Constitution. Part V. The Structure of "Liquid Crystals".—By Susil Kumar Ray ... 194
36. Negative Ferric Hydroxide Sol. A Modified Method of its Preparation.—By Ashutosh Das and Rajendrlal De ... 197
37. On the Physico-chemical Properties of Electrodialysed Gels of Silica, Alumina, Ferric Hydroxide and their Mixtures. Part I. Ion Exchange.—By Promode Behari Bhattacharyya and Kalipada Ganguli 204
38. A Note on the Constitution of the Reduction Product of Trichloromethylparaconic Acid.—By (Late) A. N. Meldrum and R. D. Kotwal 213

PAGE

39. Thermo-ageing of Colloids. Part I. Variation of Refractivity.—By Shridhar Sarvottam Joshi and P.V. Jagannatha Rao 217

40. Experiments on Resolution of Co-ordinated Inorganic Compounds into Optical Isomers. Co-ordinated Cadmium Compounds with Racemic and Active Propylenediamine.—By Panchanan Neogi and Kanai Lal Mandal 224

41. Condensation of 3- and 4-Nitrophthalic Anhydrides with Phenol and Anisole.—By P. C. Mitter and Phanindra Nath Dutt 228

42. Studies in the *iso*Flavone Series.—By P. C. Mitter and S. S. Maitra 236

43. Molecular Size of Cellulose from Different Sources. Part I. —By J. K. Chowdhury and T. P. Bardhan ... 240

44. Quinazolines. Part IV.—By Sant Singh Bedi and Kartar Singh Narang 253

45. Investigation on the Effects of Humidity and High Temperature on the NH_2-content of Different Samples of Rice.—By N. M. Basu and S. R. Maitra ... 255

46. Quinoline Derivatives. Part IV.—By Kartar Singh Narang, Jnanendra Nath Rây and Thakur Das Sachdeva ... 260

47. Chemical Examination of *Cuscuta Reflexa*, Roxb. Part. III. The Constitution of the Oil from the Seeds.—By Radha Raman Agarwal and Sikhibhushan Dutt ... 264

48. Studies on Cyclic Thioketones. Part I. Synthesis of Nonpolymerised Thio*cyclo*hexanone, Thio*cyclo*pentanone and their Derivatives.—By Dines Chandra Sen ... 268

49. Diamagnetic Susceptibilities of Tin in Di and Tetra Valency States.—By S. S. Bhatnagar, M. B. Nevgi and R. L. Sharma 273

50. Studies in the Cotarnine Series. Part VI. Condensation of Cotarnine with Phosgene.—By B. B. Dey and (Miss) P. Lakshmi Kantam 281

51. Influence of Dilution on the Molecular Refractivities of Complex Cyanides and Cobalt Ammines.—By Abani K. Bhattacharya 284

52. Measurement of Molecular Areas of Cellulose from Different Sources by Surface Tension Method. Part II. —By J. K. Chowdhury and T. P. Bardhan ... 294

PAGE

53. Use of Vanadous Sulphate as a Reducing Agent. Part II. Estimation of Chlorates, Nitrates and Persulphates.—By Pares Chandra Banerjee ... 301

54. Studies in Organo-Arsenic Compounds. Part III.—By Hirendra Nath Das-Gupta 305

55. Studies in the Coagulation of Colloids. Part XII. "Zonal effect" in the Change of Refractivity during Mutual Coagulations.—By Shridhar Sarvottam Joshi and K. P. N. Panikkar 309

56. Studies in the Coagulation of Colloids. Part XIII. "Zonal effect" in the Opacity Changes in the Coagulation of Colloid Manganese Dioxide.—By Shridhar Sarvottam Joshi and S. Jaya Rao 311

57. Analytical Uses of Nessler's Reagent. Quantitative Estimation of Monosaccharides and Disaccharides. Estimation of Furfural. Part II.—By M. Goswami and B. C. Das-Purkayastha 315

58. Syntheses in Furan Series. Part I. Synthesis of 2-Ketotetrahydrofuran-4-acetic Acid.—By Ranajit Ghosh ... 323

59. A Critical Examination of Pascal's Value for the Magnetic Susceptibility of the CH_2-Group.—By S. S. Bhatnagar and N. G. Mitra 329

60. Preparation of Compounds Related to Phenacetin.—By (Miss) B. N. Katrak 334

61. Studies in the Cotarnine Series. Part VII. Action of Sulphuric Acid on Cotarnine. Formation of Methylene-*bis*phenol-betain of 2-Methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro*iso*quinolinium Hydroxide.—By B. B. Dey and T. K. Srinivasan 337

62. Chemical Examination of the Fixed Oil from the Seeds of *Celastrus Paniculatus*, Willd.—By O. N. Kumaraswamy and B. L. Manjunath 353

63. *C*-Alkyl Resorcinols. Part II. Synthesis of Polyalkyl Resorcinols.—By R. C. Shah and P. R. Mehta ... 358

64. A New and Convenient Synthesis of 2 : 4-Dihydroxybenzophenone.—By R. C. Shah and P. R. Mehta ... 368

65. Variation of the Cataphoretic Velocity of Colloidal Particles during Aggregation. Part I.—By Jnanendra Nath Mukherjee, Subodh Gobinda Chaudhury and Krishnadhan Bhabak 372

PAGE

66. Peroxidases. Part III. A Potentiometric Method of Estimating their Activity.—By B. B. Dey, S. Rengachari and M. V. Sitharaman 390
67. New Compounds of Gallium. Part I.—By Panchanan Neogi and Sarajit Kumar Nandi 399
68. Oxidation of Acetyltetrahydroquinoline Sulphonic Acids.—By K. V. Bokil 404
69. On Activated Charcoal. Part II. Purification by Washing with Water and by Activation.—By Satyaprasad Roychoudhury, Sarajit Kumar Nandi and Jiban Krishna Banerjee 410
70. A Synthesis of *cis*- and *trans-dl-iso*Propyl*cyclo*propane-1 : 2-dicarboxylic Acid and Experiments towards the Resolution of the *cis-dl*-Acid.—By S. K. Ranganathan 419
71. On the Fluorination of Organic Compounds. Part II.—By P. C. Rây and Anil Chandra Ray 427
72. Variation of Cataphoretic Velocity of Colloidal Particles during Aggregation. Part II.—By Jnanendra Nath Mukherjee, Subodh Gobinda Chaudhury and Jyotirmoy Sen-Gupta 428
73. Studies in the Coagulation of Colloids. Part XIV. Coagulation of Colloid Arsenious Sulphide by Mercuric Chloride. Inadmissibility of Viscosity and Transparency as General Criteria of Coagulation.—By Shridhar Sarvottam, Joshi and Sadashiv S. Kulkarni ... 439
74. Studies in the Anthraquinone Series. Attempts to synthesise Anthraquinone Carboxylic Acids of the Morindone Type.—By P. C. Mitter and (Miss) Tanima Sen-Gupta 447
75. The Enzymes in Snake-venom. Part I. Their Action on Hæmoglobin and on Protein Solutions of different *p*H—By B. N. Ghosh 450
76. On the Study of Polyhalides. Part IV. Formation and Dissociation of Polyhalides of Ammonium and Substituted Ammonium Bases.—By Susil Kumar Ray and Rama Ranjan Bhattacharya 456
77. Attempts to Prepare Ring Glycerides. Preparation of Tetrachlorodiglycerides of Dicarboxylic Acids.—By M. Goswami and A. Shaha 464

PAGE

78. The Rotatory Powers of Substituted Camphoranilic Acids.—By Mahan Singh 467

79. Chloral Derivatives of Salicylic Acid.—By Narshinh Muljibhai Shah and Rupchand Lilaram Alimchandani ... 475

80. Methoxy-oxypalmatine.—By Narindra Nath Chopra and Jnanendra Nath Rây 478

81. Studies in the Acenaphthenequinone Series. Part II.—By Anukul Chandra Sircar and Sailesh Chandra Sen ... 482

82. Parachor and the Structure of Formic Acid.—By Susil Kumar Ray 484

83. A Note on the Use of Adsorption Indicators in Acidimetry and Alkalimetry.—By Sachindra Nath Roy ... 486

84. A Magnetic Study of Colour Changes in Cobalt Chloride. Part II.—By S. S. Bhatnagar, A. N. Kapur and P. L. Kapur 489

85. Complex Metal-ammonium Selenites and Selenito-metal-ammines.—By Priyadaranjan Rây and Amalendra Narayan Ghosh 494

86. Oxidation of Glucose in presence of Insulin, Glutathione and other Substances and the Probable Mechanism of Biological Oxidations.—By C. C. Palit and N. R. Dhar 502

87. Synthesis in the Pyrazolone Series. Part IV. Action of Aminoguanidines on β-Ketonic Esters and β-Diketones. —By S. C. De and P. C. Rakshit 509

88. An *X*-Ray Investigation of the Crystals of *p*-Nitrodiphenyl.—By Mata Prasad, M. P. Lakhani and Jagdish Shanker 519

89. Studies in the Camphor Series. Part III. Tautomeric Behaviour of Thiocamphor and the Activity of its Sodium Derivative.—By Dines Chandra Sen ... 523

90. The Quaternary Ammonium Iodides of Dimethyl-*p*-toluidine.—By M. Q. Doja 527

91. Chemical Examination of *Cuscuta Reflexa,* Roxb. Part IV. Isolation of a New Yellow Flavone Colouring Matter from the Seeds.—By Radha Raman Agarwal ... 531

92. Spiro-compounds. Part I. A New Route to Spiro-compounds. Synthesis of *cyclo*Hexane-spiro-*cyclo*-pentane.—By Nripendra Nath Chatterjee ... 536

PAGE

93. Preparation of *p*-Diethylaminobenzaldehyde.—By M. Q. Doja and A. Mokeet 542

94. Removal of Antimony from its Solutions by Nitric Acid.—By M. B. Rane, K. Kondaiah and M. K. Ratnam 544

95. A Note on the Estimation of Formic Acid in Commercial Acetate of Lime.—By S. D. Sunawala ... 545

96. On the Physico-chemical Properties of Electrodialysed Gels of Silica, Alumina, Ferric Hydroxide and their Mixtures. Part II. Moisture Retention Capacity of the Gels Saturated with different Cations.—By Promode Behari Bhattacharyya and Kalipada Ganguli 547

97. Denitrification in Sunlight and its Retardation. Part III. —By N. R. Dhar and S. K. Mukerji 555

98. Investigations on Cod Liver Oil Emulsions. Antagonism of Emulsifying Agents.—By Nirmalapada Chatterjee... 563

99. Dyes Derived from Isatin. Azines and Indigoid Vat Dyes. —By Sisir Kumar Guha and Hariprasad Basu-Mallick 571

100. Râman Effect and Molecular Structure. Part I. The Structure of the Guanidinium Ion.—By Jagannath Gupta 575

101. Studies on the Addition of Hydrogen Halides to Butadiene. —By S. N. Ganguly 580

102. The Constitution of Ayapanin.—By Prafulla Kumar Bose and Anil Chandra Roy 586

103. Spiro-compounds. Part II. Ring Transformation in Spiro-compound from 4-Methyl*cyclo*hexanone. A New Synthesis of Cadalene.—By Nripendra Nath Chatterjee 588

104. Synthesis of Diphenyl Acetates.—By Nripendra Nath Chatterjee 593

105. On Phthalide Formation.—By Prafulla Kumar Paul ... 599

106. Preparation and Properties of Highly Concentrated Sols. Part V. Stannic Hydroxide Sols.—By N. R. Dhar and Ch. I. Varadanam... 602

PAGE

107. Derivatives of 1-Hydroxy-2-naphthoic Acid. Part I. 4-Halogeno-1-hydroxy-2-naphthoic Acid and their Derivatives.—By G. V. Jadhav, S. N. Rao and N. W. Hirwe 609

108. The Chemical Examination of *Solanum Xanthocarpum*, Schard and Wendel. Part I. The Constituents of the Oil from the Seeds.—By Mahadeo Prasad Gupta and Sikhibhushan Dutt 613

109. Synthesis of Coumarins and Chromones from Halogenated and Nitrocresols.—By Duhkhaharan Chakravarti and Bhawani Charan Banerjee 619

110. The Enzymes in Snake-venom. Part II. Their Action on Native Proteins, on Peptone and on the Activity of Trypsin —By B. N. Ghosh and S. S. De 627

111. Constituents of the Leaves of *Vitex Negundo*.—By T. P. Ghose and S. Krishna 634

112. 6-Sulpho-*m*-cresotic Acid and Related Compounds.—By (Late) A. N. Meldrum and C. N. Bamji ... 641

113. Derivatives of 1-Hydroxy-2-naphthoic Acid. Part II. 4-Halogeno-1-methoxy-2-naphthoic Acids and their Derivatives.—By G. V. Jadhav and S. N. Rao ... 645

114. Synthesis of Coumarins and Chromones from 4-Chloro- and 4-Bromo-1-naphthol.—By Duhkhaharan Chakravarti and Phanindra Nath Bagchi 649

115. A Note on Solid Sugars from Mohuwa Flower Syrup.—By D. G. Walawalkar 657

116. Phenanthrene from 9-Hydroxyphenanthrene (A note).—By Nripendra Nath Chatterjee 659

117. *X*-ray Investigation of the Crystals of *o*-Nitrodiphenylamine.—By Mata Prasad and Jagdish Shanker ... 663

118. On the Relation between Peptisation of a Precipitate and its Electrokinetic Potential.—By Subodh Gobinda Chaudhury and Jyotirmoy Sen-Gupta 670

119. Adsorptive Properties of Synthetic Resins.—By S. S. Bhatnagar, A. N. Kapur and M. L. Puri ... 679

120. On the Limited Applicability of Kostanecki's Reaction.—By Duhkhaharan Chakravarti and Phanindra Nath Bagchi 689

PAGE

121. The Action of Hydrogen Sulphide on Mercurous Chromate.—By M.A. Hamid, V. S. Bhatia and H B. Dunnicliff 697

122. On some Synthetic Compounds related to Atophan.—By Prafulla Kumar Bose and Nirmal Chandra Guha ... 700

123. Condensations of Furil and Furoin.—By Anukul Chandra Sircar and Sudhangsu Chandra Guha 704

124. Studies in Acenaphthenequinone Series. Part III.—By Anukul Chandra Sircar and Dwipendra Chandra Chowdhury 709

125. Potentiometric Studies in Oxidation-reduction Reaction. Part I. Oxidation with Potassium Iodate.—By Balwant Singh and Ijaz Ilahi 717

126. Properties of Activated Sugar Charcoal Coated with Various Substances. Part I. Liberation of Acid and Alkali by the Action of Neutral Salts in Relation to the Surface Charge.—By Harendra Kumar Acharya 723

127. Dihydroresorcinols. Part IV. The Condensation of Phenyldihydroresorcinol with Aromatic Aldehydes.—By R. D. Desai and M. A. Wali 735

128. Studies in Vitamin C. Part II. The Vitamin C Contents of the Liver and Muscle of some Indian Fresh-water Fish.—By Mahendra Nath Rudra 740

129. Studies on Optical Activity and Chemical Constitution. Part III. Optically Active Acids and Bases.—By Mahan Singh and Manohar Singh 743

130. A New Method for the Separation of Lead from Copper and their Subsequent Estimations.—By K. M. Sil, G. C. Roy and P. N. Das-Gupta 747

131. Estimation of Small Quantities of Arsenic in Medicolegal Cases.—By D. N. Chatterji, K. R. Ganguly and M. Z. Faruqi 751

132. Studies in the Coagulation of Colloids. Part XV. New Aspects of Gold Sol Coagulation.—By Shridhar Sarvottam Joshi and N. Hanumantha Rao ... 755

Reviews 74, 350, 546, 660

Obituary 345

JOURNAL

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Oxidation of Monochloroacetic Acid by Potassium Permanganate at Wave-lengths 366 $\mu\mu$ and 436 $\mu\mu$ with Uranyl Salt as Photosensitiser.

By J. C. Ghosh and B. B. Ray.

In a previous paper Ghosh, Narayanmurti and Ray (*Z. physikal. Chem.*, 1935, **B 29**, 236) published the results of an investigation on the oxidation of mandelic acid by methylene blue with uranyl nitrate as photosensitiser. Mandelic acid is easily oxidised into phenylpyruvic acid which decomposes to produce benzaldehyde. It was found that almost every collision between the excited uranyl ion with mandelic acid results in this oxidative change. In this paper, the photo-oxidation of monochloroacetic acid, which is a much stabler compound, has been studied using potassium permanganate as the oxidant.

The experimental arrangement is the same as described in the previous paper, the source of light being a point-source quartz mercury lamp from which parallel beams of light were obtained by using quartz lenses. The reaction cells were made of fused quartz plates sealed into one another without cement and had the dimensions 1·8 cm. × 1·8 cm. × 0·5 cm. The following filters were used for monochromatism :

436 $\mu\mu$—Schott and Gen Blue filter (U.4) + 2 cm. of 2% copper sulphate solution in water.

366 $\mu\mu$—Chance Bros. U. V. filter (1 mm.) + 2 cm. of 2% copper sulphate solution in water.

The liquid filters were contained in quartz cells and were placed between the lens and the reaction cell.

The course of reaction was followed by observing the change in concentration of potassium permanganate. The concentration in the reaction cell was measured by observing the absorption of light at

540 $\mu\mu$ with the aid of a König-Marten spectrophotometer. At the concentration used, the uranyl sulphate in the mixture does not perceptibly affect the spectrophotometric readings. On plotting the values of log tan θ, (θ being the spectrophotometric angle) against the corresponding concentration of $KMnO_4$, a straight line was obtained. In any experiment, therefore, the observed value of θ at any moment becomes a measure of the concentration of $KMnO_4$ at that moment.

EXPERIMENTAL.

Rideal and Norrish (*Proc. Roy. Soc.*, 1923, **A, 103**, 342) have shown that ultraviolet light of wave-length 366 $\mu\mu$ as also visible light, have no action on a solution of potassium permanganate.

No change in concentration of potassium permanganate was also observed when (*i*) a mixture of 0·0005M-$KMnO_4$ and 0·1M-monochloroacetic acid was illuminated by light of $\lambda = 366\ \mu\mu$, or (*ii*) when a mixture of 0·1 M-uranyl sulphate and 0·0005 M-$KMnO_4$ was similarly exposed.

Also, no reaction was found to take place when a mixture of potassium permanganate, monochloroacetic acid and uranyl sulphate was kept in the dark.

When, however, the mixture was exposed to radiation 366 $\mu\mu$, there was gradual decolourisation of potassium permanganate showing that reaction was taking place. The reaction is purely zero-molecular with respect to $KMnO_4$.

The following is a typical example.

$\triangle x/\triangle t$ gives the number of g. molecules of $KMnO_4$ reacting per unit area of the solution of 5 mm. thickness per sec. There is no induction period.

TABLE I*a*.

$KMnO_4$ conc. = 0·00051M. $CH_2ClCOOH$ conc. = 0·1M. UO_2SO_4 conc. = 0·1M. H_2SO_4 conc. = 2·5N.

Temp. = 30°. Incident intensity = 2650 ergs/sec. cm^2. at 366 $\mu\mu$.

Time.	Spectrophoto reading.	Conc. of $KMnO_4$.	$\frac{\Delta x}{\Delta t} \times 10^{11}$.
0 sec.	65·5	$5{\cdot}0 \times 10^{-4}M$	
3600	61·5	$3{\cdot}9 \times 10^{-4}$	1·5
4860	60·5	$3{\cdot}6 \times 10^{-4}$	1·4
7200	57·5	$2{\cdot}8 \times 10^{-4}$	1·5
8580	56·0	$2{\cdot}4 \times 10^{-4}$	1·5
		Mean	1·5

TABLE I*b*.

$KMnO_4$ conc.=0·00042*M*. $CH_2ClCOOH$ conc.=0·03*M*.
UO_2SO_4 conc.=0·1*M*. H_2SO_4 conc.=3*N*.
Temp.=30°. Incident intensity=930 ergs/sec. cm² at 436 $\mu\mu$.

Time.	Spectrophoto reading.	Conc. of $KMnO_4$.	$\frac{\Delta x}{\Delta t} \times 10^{11}$.
0 sec.	64·0	$4·5 \times 10^{-4}M$	
4740	62·7	$4·2 \times 10^{-4}$	0·32
8760	61·7	$3·9 \times 10^{-4}$	0·34
		Mean	0·33

The radiation absorbed by uranyl sulphate in the mixture which is the only photo-active material in the system was calculated by the approximate formula,

$$I_{abs} = I_0 \left[1 - e^{-\epsilon_1 c_1 d - \epsilon_2 c_2 d}\right] \frac{\epsilon_1 c_1}{\epsilon_1 c_1 + \epsilon_2 c_2} \quad \ldots \quad (i)$$

where I_0 =intensity of incident radiation, measured by Moll galvanometer and thermopile ; ϵ_1=enhanced extinction coefficient of uranyl sulphate in presence of monochloroacetic acid ; c_1=concentration of uranyl sulphate ; ϵ_2=extinction coefficient of potassium permanganate and c_2=concentration of potassium permanganate.

The extinction coefficients were measured by means of a Moll galvanometer and thermopile, calibrated against a standard Hefner lamp tested by the Bureau of Standards. The intensities of light incident and transmitted through the solution were measured and the molar extinction coefficient determined from the equation

$$\epsilon = \frac{\log_e I_0 - \log_e I_t}{c.d.}$$

where *c* is the concentration of the solution and *d*, the thickness.

Table II gives the extinction coefficient of potassium permanganate in sulphuric acid solution at wave-length 366 $\mu\mu$.

TABLE II.

$KMnO_4$ conc.	d.	I_0.	Radiation transmitted I_t.	ϵ.
$6{\cdot}8 \times 10^{-4}M$	0·5 cm.	3080 ergs	1600 ergs	1900
$2{\cdot}3 \times 10^{-4}$	0·5	3080	2450	2020
$3{\cdot}0 \times 10^{-4}$	1·0	2100	1130	2050
			Mean	2000

This value of the extinction coefficient of $KMnO_4$ was verified by taking photographs of absorption spectra of a $4{\cdot}7 \times 10^{-4}M$ solution of $KMnO_4$ by means of a Hilger spectrograph with a rotating sector. From the absorption curve the value of $1/d \log_{10} I_o/I_t$ at wavelength 366 $\mu\mu$ was found to be 0·38, so that

$$\epsilon = \frac{1}{c.\ d} \log I_o/I_t = 1860$$

At 436 $\mu\mu$, $\frac{1}{d} \log_{10} I_o/I_t = 0{\cdot}045$. $\therefore \ \epsilon = 220$.

The experimental results are recorded below.

TABLE III.

Composition of solution.	Extinction coefficient ϵ at $\lambda = 436\ \mu\mu$.	$\lambda = 366\ \mu\mu$.
$KMnO_4$	220	2000
UO_2SO_4 in presence of excess of $CH_2ClCOOH$	6·5	10

It will be noted that a zero-molecular velocity constant, that is, a constant velocity of reaction as indicated by the rate of disappearance of $KMnO_4$ must lead to the conclusion that the radiant energy absorbed by the uranyl ion in solution is independent of the relative concentration of $KMnO_4$ and its reduction product; that is in equation (*i*), $\epsilon_2 c_2$ is practically constant, whether it be due to $KMnO_4$ or a mixture of $KMnO_4$ and its reduction product.

This was verified in the following way. To a definite concentration of $KMnO_4$ in sulphuric acid, different concentrations of oxalic acid were added, there being excess of permanganate in each case, and the absorption of the solutions were measured. The radiation 366 $\mu\mu$ absorbed were found to be practically the same in all cases.

TABLE IV.

Comp. of soln. (5 mm. thick)	Conc. of $KMnO_4$ in the mixture.	Incident intensity.	Radiation absorbed.
2 c.c. 0·00245*M*-$KMnO_4$ 5 c.c. 5*N*-H_2SO_4 2 c.c. water	$5{\cdot}4 \times 10^{-4}$ *M*	3000 ergs	1140 ergs
2 c.c. 0·00245*M*-$KMnO_4$ 5 c.c. 5*N*-H_2SO_4 0·5 c.c. 0·01*N*-oxalic acid 1·5 c.c. water	$4{\cdot}25 \times 10^{-4}$	Do.	1120
2 c.c. 0·00245 *M* $KMnO_4$ 5 c.c. 5*N*-H_2SO_4 1 c.c. 0·01 *N*-oxalic acid 1 c.c. water	$3{\cdot}2 \times 10^{-4}$	Do.	1110

This result was confirmed by taking photographs of absorption spectra of the following solutions by means of a Hilger spectrograph with a rotating sector.

TABLE V.

Composition of solution.	Conc. of $KMnO_4$ in the mixture.
10 c.c. 0·00235*M*-$KMnO_4$ 20 c.c. 7 *N*-H_2SO_4 20 c.c. water	$4{\cdot}7 \times 10^{-4}$ *M*
10 c.c. 0·00235 *M*-$KMnO_4$ 20 c.c. 7 *N*-H_2SO_4 2 c.c. 0·01 *N*-oxalic acid 18 c.c. water	$3{\cdot}9 \times 10^{-4}$
10 c.c. 0·00235 *M*-$KMnO_4$ 20 c.c. 7 *N* H_2SO_4 5 c.c. 0·01 *N*-oxalic acid 15 c.c. water	$2{\cdot}65 \times 10^{-4}$

The three absorption curves of the solutions were found to be practically identical, which confirms the view that in reaction of $KMnO_4$ with monochloroacetic acid, the value of $\epsilon_2 c_2$ in equation (*i*) remains practically constant.

Effect of Conc. of Monochloroacetic Acid on the Velocity of Reaction.—The velocity of reaction was found to be dependent on the conc. of monochloroacetic acid, decreasing with decrease in concentration of the acceptor. The reciprocal of the velocity plotted against the reciprocal of concentration of $CH_2ClCOOH$ gave a straight line.

TABLE VI.

$KMnO_4$ conc. = 4·2 × $10^{-4}M$. UO_2SO_4 conc. = 0·087M. H_2SO_4 conc. = 3N. Temp. = 29°. λ = 436$\mu\mu$.

I_0 = 1030 ergs. Energy absorbed by UO_2SO_4 = 250 ergs. No. of quanta absorbed/sec. cm^2 = 5·5 × 10^{13}.

Conc. of $CH_2ClCOOH$	...	0·033 M	0.05M	0·1M	0·2M
$\frac{\Delta x}{\Delta t} \times 10^{11}$	...	0·34	0·43	0·57	0·66
Quantum efficiency	...	0·038	0·048	0·063	0·073

The significance of these results will be discussed later.

Influence of the Energy of Radiation absorbed by the Photosensitiser and the Concentration of the Photosensitiser on the Velocity of Reaction.—The velocity of reaction increases with increase in concentration of the sensitiser UO_2SO_4, until at higher concentration it becomes practically constant. In the fifth column of Table VII are given the calculated velocity of reaction according to the equation

$$\frac{\Delta x}{\Delta t} = K_0 \frac{I_{abs} \text{ by } \mathrm{U\ddot{O}_2}}{1 + 9{\cdot}08[\mathrm{U\ddot{O}_2}]} \qquad \dots \quad (ii)$$

TABLE VII.

$CH_2ClCOOH$ conc. = 0·1 M. $KMnO_4$ conc. = 4·2 × $10^{-4}M$. H_2SO_4 conc. = 3N. Temp. = 29°.

(*a*) Incident intensity = 1030 ergs/sec. cm^2. at λ = 436 $\mu\mu$.

1. Conc. of UO_2SO_4.	2. Radiation absorbed by UO_2SO_4	3. No. of quanta absorbed/sec. cm^2.	4. $\frac{\Delta x}{\Delta t} \times 10^{11}$ Obs.	5. Vel. calc. from eq. (*ii*).	6. Quantum efficiency.
0·0218 M	70 ergs	1·57 × 10^{13}	0·26	0·24	0·10
0·0436	134	3·0 × 10^{13}	0·38	0·40	0·077
0·0653	193	4·3 × 10^{13}	0·47	0·49 taking K_0 = 4·1 × 10^{-3}	0·067
0·0871	249	5·5 × 10^{13}	0·57	0·57	0·063
0·1511	373	8·3 × 10^{13}	0·68	0·65	0·05
0·2267	526	11·9 × 10^{13}	0·70	0·70	0·036

TABLE VII (*contd.*)

(*b*) Incident intensity = 3360 ergs/sec. cm^2. at $\lambda = 366\mu\mu$.

1.	2.	3.	4.	5.	6.
0·0218 *M*	283 ergs	$0{\cdot}53 \times 10^{14}$	1·02	0·94	0·12
0·0436	540	$1{\cdot}0 \times 10^{14}$	1·47	1·50	0·09
0·0653	770	$1{\cdot}4 \times 10^{14}$	1·89	1·88 taking $K_0 = 3{\cdot}9 \times 10^{-3}$	0·082
0·0871	975	$1{\cdot}8 \times 10^{14}$	2·05	2·12	0·07
0·1511	1490	$2{\cdot}8 \times 10^{14}$	2·29	2·40	0·05
0·2267	1925	$3{\cdot}6 \times 10^{14}$	2·45	2·45	0·042

Velocity Constant and Intensity of Incident Light.—The intensity of incident radiation was varied by using quartz lenses of different focal lengths.

TABLE VIII.

$KMnO_4$ conc. = $5{\cdot}1 \times 10^{-4}$ *M*. $CH_2ClCOOH$ conc. = 0·1 *M*.
H_2SO_4 conc. = 2·6 *N*. Temp. = 29°.

Conc. of UO_2SO_4.	I_0 at $366\mu\mu$.	$K_0 \times 10^{11}$.	I'_0 at $366\mu\mu$.	$K'_0 \times 10^{11}$.	$\frac{I_0}{I'_0}$	$\frac{K_0}{K'_0}$.
0·05 *M*	4190 ergs	1·98	2650 ergs	1·21	1·58	1·63
0·1	4190	2·33	2650	1·49	1·58	1·56

It will thus be seen that with other experimental factors remaining the same, the velocity of reaction is directly proportional to the intensity of incident radiation.

Temperature Coefficient.

TABLE IX.

$KMnO_4$ conc. = $5{\cdot}2 \times 10^{-4}M$. $CH_2ClCOOH$ conc. = 0·08*M*.
H_2SO_4 conc. = 2·8 *N*. $I_0 = 2870$ ergs/sec. cm^2. at $\lambda = 366\mu\mu$.

Temp.	Conc. of UO_2SO_4.	$\frac{\Delta x}{\Delta t} \times 10^{11}$.	Temp. coeff. (per 10°).
30°	0·067 *M*	1·23	1·02
40°	,,	1·26	
30°	0·0335	1·01	1·04
40°	,,	1·05	

Temperature coefficient is thus approximately equal to unity.

DISCUSSION.

From the experimental results it follows that any mechanism of reaction that may be proposed for this photo-sensitised oxidation, should be in a position to explain the following facts :

(*i*) The velocity of reaction is zero-molecular with respect to potassium permanganate.

(*ii*) With other factors remaining constant, the reciprocal of the velocity of reaction plotted against the reciprocal of the concentration of monochloroacetic acid, is a straight line.

(*iii*) The velocity of reaction is directly proportional to the intensity of incident radiation.

(*iv*) The velocity of reaction is influenced by change in concentration of uranyl sulphate, according to the following equation

$$\frac{\triangle x}{\triangle t} = K_0 \cdot \frac{I_{\text{abs}} \text{ by } UO_2^{\cdot\cdot}}{1 + 9{\cdot}08[UO_2^{\cdot\cdot}]}$$

when concentration of monochloroacetic acid is $0{\cdot}1M$.

All these characteristics can be explained if we assume the following mechanism of reaction.

$$UO_2^{\cdot\cdot} + h\nu \rightarrow UO_2^{\cdot\cdot *} \text{ [excited.]} \qquad \ldots \quad (1)$$

$$UO_2^{\cdot\cdot *} \rightarrow UO_2^{\cdot\cdot} + \text{ fluorescent radiation} \qquad \ldots \quad (2)$$

$$UO_2^{\cdot\cdot *} + UO_2^{\cdot\cdot} \rightarrow 2UO_2^{\cdot\cdot} \qquad \ldots \quad (3)$$

$$UO_2^{\cdot\cdot *} + CH_2ClCOOH \longrightarrow UO^{\cdot\cdot} + \text{oxidation product} \qquad \ldots \quad (4)$$

$$UO^{\cdot\cdot} + KMnO_4 \rightarrow UO_2^{\cdot\cdot} + \text{ reduction product} \qquad \ldots \quad (5)$$

Equating the stationary concentration of $UO^{\cdot\cdot *}_2$, we get for the velocity of oxidation of monochloroacetic acid the following equation :—

$$\frac{\triangle x}{\triangle t} = \frac{I_{\text{abs}} \text{ by } UO_2^{\cdot\cdot}}{Nh\nu} \cdot \frac{k_4[\text{Mc}]}{k_2 + k_3[UO_2^{\cdot\cdot}] + k_4[\text{Mc}]} \qquad \ldots \quad (a)$$

where [Mc] is the conc. of monochloroacetic acid.

The fluorescence of uranyl salts has been studied by Wawilow (*Z. Physik*, 1928, **50**, 56). Reactions (1), (2) and (3) above, give the mechanism of fluorescent radiation in pure aqueous solution. The intensity of fluorescent radiation was found by Wawilow to be quantitatively expressed by the equation

$$\frac{1}{L} = \frac{1}{L_0} + 3{\cdot}45 \times 10^2 C \qquad \ldots \quad (b)$$

where C is the concentration of uranyl salt in g./c.c., L is the observed fluorescent intensity and L_0 is the limiting value of the fluorescent intensity when the conc. of uranyl salt is infinitely small, that is, reaction (3) does not take place. Under this limiting condition, every $\ddot{\mathrm{U}}\mathrm{O}_2$-ion excited by absorbed radiation re-emits the same as fluorescent radiation. We may write equation (b) in the form

$$L = \frac{L_0}{1 + 3{\cdot}45 \times 10^2 C\, L_0} \qquad \ldots \quad (c)$$

$$\text{or} \qquad L = \frac{L_0}{1 + 2{\cdot}84 \times 10^2 C}$$

Since L_0 was found to have the experimental value 0·82.

If C be expressed in g. mol/litre, $L = \dfrac{L_0}{1 + 99[\ddot{\mathrm{U}}\mathrm{O}_2]}$ ... (d)

Now considering reactions (1), (2) and (3) above, we get

$$L = \frac{I_{\text{abs}} \text{ by } \ddot{\mathrm{U}}\mathrm{O}_2}{Nh\nu} \cdot \frac{k_2}{k_2 + k_3 [\ddot{\mathrm{U}}\mathrm{O}_2]}$$

$$= \frac{I_{\text{abs}}}{Nh\nu} \cdot \frac{1}{1 + k_3/k_2 [\ddot{\mathrm{U}}\mathrm{O}_2]}.$$

From Wawilow's experimental data on the emission of fluorescent radiation by uranyl salts, it is, therefore, possible to find out the value of k_3/k_2, which from equation (d) is equal to 99

$$\text{or } k_3 = 99\, k_2.$$

The values of k_3 and k_4, which depend upon the kinetic collision, have practically the same magnitude, if we assume that each collison between the excited ion of $\ddot{\mathrm{U}}\mathrm{O}_2$ and a normal $\ddot{\mathrm{U}}\mathrm{O}_2$-ion or a monochloroacetic acid molecule leads to chemical transformation.

$$\text{Hence } k_4 = k_3 = 99\, k_2.$$

Equation (a) may, therefore, be written as

$$\frac{\Delta x}{\Delta t} = \frac{I_{abs} \text{ by } U\ddot{O}_2}{Nh\nu} \cdot \frac{k_4\,[Mc]}{k_2 + k_4\,[Mc]} \cdot \frac{1}{1 + \dfrac{k_3\,[U\ddot{O}_2]}{k_2 + k_4\,[Mc]}}$$

$$= \frac{I_{abs}}{Nh\nu} \cdot \frac{k_4\,[Mc]}{k_2 + k_4\,[Mc]} \cdot \frac{1}{1 + 9{\cdot}08\,[U\ddot{O}_2]} \quad \ldots \quad (e)$$

(where the conc. of $CH_2ClCOOH$ is $0{\cdot}1$ M).

$$= \frac{k}{Nh\nu} \cdot \frac{I_{abs}}{1 + 9{\cdot}08\,[U\ddot{O}_2]} \text{ where } K = \frac{k_4\,[Mc]}{k_2 + k_4\,[Mc]}.$$

The values of K_0 recorded in Table VIII are, therefore, identical with $k/Nh\nu$. Again from equation (a)

$$\frac{\Delta t}{\Delta x} = \frac{Nh\nu}{I_{abs}} + \frac{Nh\nu}{I_{abs}} \cdot \frac{k_2 + k_3\,[U\ddot{O}_2]}{k_4\,[Mc]}.$$

Thus the values of $[U\ddot{O}_2]$ and I_{abs} remaining constant, the reciprocal of velocity, $\Delta t/\Delta x$, plotted against the reciprocal of concentration of monochloroacetic acid should give a straight line and this has been found to be the case.

Quantum Efficiency.—Equation (e) indicates that the quantum efficiency of the oxidation of monochloroacetic acid, which is equal to $\Delta x/\Delta t \big/ I_{abs}/Nh\nu$ will be dependent on the concentration of monochloroacetic acid. For large concentration of the acid, the value of $k_4\,[Mc]/k_2 + k_4\,[Mc]$ becomes practically equal to unity, so that equation (e) reduces to the form

$$\frac{\Delta x}{\Delta t} = \frac{I_{abs}}{Nh\nu} \cdot \frac{1}{1 + 9{\cdot}08\,[U\ddot{O}_2]}.$$

The quantum efficiency gradually falls off with increasing concentration of uranyl sulphate, as more and more of the light absorbed is dissipated by collision of the second kind.

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Action of Dyestuffs and other Substances on Milk Dehydrogenase. Identity of Schardinger Enzyme with Xanthine Oxidase.

By Kali Pada Basu and Sati Prasad Mukherjee.

The oxidising enzymes in milk have been the subject of intensive investigation by the Cambridge School and lately also by Wieland and his collaborators. There is a fundamental difference of opinion between the Cambridge School and Wieland with regard to these oxidising enzymes. Although Morgan, Stewart and Hopkins (*Proc. Roy. Soc.*, 1922, **B 94**, 909) doubted that one and the same enzyme should be able to oxidise two substances of such widely different nature as xanthine and aldehydes, later observations and publications from the Cambridge School have always supported the view that one and only one enzyme is responsible for oxidising both the substances. Wieland, on the other hand, maintains that two different enzymes in milk are responsible for the oxidation of the substances of the purine group and the aldehydes. The experimental evidences from the two laboratories might be briefly discussed.

Dixon and Thurlow (*Biochem. J.*, 1924, **18**, 976) were unable by any means to effect a separation of the enzymes and found by comparing a large number of enzyme preparations from different milks, a striking parallelism between the two activities. The *p*H curves of the two reactions were found to be very similar. Uric acid was found to inhibit both the aldehyde and the xanthine oxidation in the similar manner. Wieland and Rosenfeld (*Annalen*, 1930, **77**, 32) found that the ratio between the xanthine oxidation capacity and salicylaldehyde oxidation capacity increased on keeping and more quickly on shaking the milk (Wieland and Macrae, *Annalen*, 1930, **483**, 217). The power of milk to oxidise xanthine gradually increased, whereas the power to oxidise aldehyde practically remained constant. Dixon and Thurlow explained this as being due to the accelerating effect of fat on xanthine oxidation only. Wieland and Rosenfeld could also alter the ratio of X-E—Sa-E to about ten times by subjecting the enzyme materials to adsorption.

However, Wieland and Macrae measured the time of decolourisation of a given quantity of methylene blue by milk enzyme separately by xanthine and by salicylaldehyde and also in the presence of both the substrates. Contrary to their expectations they did not find a diminution in the time for decolourisation of the dyestuff in presence of the two substrates although both were present in optimum concentration.

Sen (*Biochem. J.*, 1931, **25**, 855) measured the absorption of oxygen by the combined system of hypoxanthine and vanillin in presence of milk enzyme and observed a somewhat less adsorption than with the more active substrate alone and attributed this to the existence of one enzyme only. Wieland and Mitchell (*Annalen*, 1932, **492**, 156) are of opinion that this might be caused by the mutual inhibitory effect of the two substrates on their adsorption on the enzyme surface. But they also failed to observe any decrease in the time of decolourisation of methylene blue by xanthine by the addition of increasing amounts of acetaldehyde.

They also thought that with quinone as the acceptor the dehydrogenation proceeded a bit more quickly in vessels containing the mixture of the two substrates than in vessels containing only one substrate. It must be remarked, however, that this summation effect is not very pronounced from their data. After the manuscript was ready another paper by Booth (*Biochem. J.*, 1935, **29**, 1732) has appeared from the Cambridge laboratory in which the identity of the two enzymes is again emphasised. Thus the whole question of the identity of the two enzymes responsible for the oxidation of purine bases and aldehydes is still open and requires further investigation.

Toxic actions of substances of known structure on an enzyme would give us some information about the nature of the active group in the latter. Investigations in this line were carried out by Bamann and Schemller (*Z. physiol. Chem.*, 1931, **194**, 1) who showed that indicators of the type phenolphthalein, bromothymol blue, etc., have a toxic action on lipase. Quastel (*Biochem. J.*, 1931, **25**, 628, 898; 1932, **26**, 1685) has tried the action of a series of acidic and basic dyes on dehydrogenase, fumarase and urease, and recently Basu and Chakravarti (*J. Indian Chem. Soc.*, 1935, **12**, 82) tried the action of various dyestuffs on proteolytic enzymes, *e.g.*, trypsin and papain. It should be possible to distinguish between apparently closely related enzymes like the different proteinases, polypeptidases, etc., by taking advantages of the specific toxic action of the dyestuffs.

The present investigation was, therefore, carried out to determine the action of a series of dyestuffs, some narcotics and certain other substances on the oxidation of xanthine and of aldehydes by milk dehydrogenase in order to find out the nature of the active group in the enzyme and also to see whether any of the investigated dyestuffs and other substances revealed any difference in behaviour towards the oxidation of these substances. It should be possible by this means to establish the identity or other wise of the Schardinger enzyme with the xanthine oxidase.

EXPERIMENTAL.

The caseinogen preparation obtained by the method of Dixon and Thurlow (*loc. cit.*) was employed as enzyme material. Attempts to prepare the cream preparation by the method of Wieland and Rosenfeld (*loc. cit. cf.* also Toyama, *Biochem. J. Japan*, 1933, **17**, 131) did not give satisfactory results. The enzyme material was preserved in the refrigerator. Absorption measurements were carried out in Barcroft-Warburg respirometers at 37°.

Determination of Optimum p_H and Optimum Concentration of the Substrate.

Using hypoxanthine and aldehydes, Dixon and Thurlow (*loc. cit.*) determined the optimum p_H and optimum concentration of the substrates with methylene blue as the hydrogen acceptor. So far as the oxidation in oxygen is concerned, very little data is available with regard to the optimum p_H and optimum substrate concentration.

Optimum p_H.—Using xanthine, salicylaldehyde and acetaldehyde with same concentration of the enzyme solution and phosphate buffer the following variation of their oxygen uptake was noted with the change of p_H.

TABLE I *a*.

Substrate—xanthine. 4 C.c. of 3% caseinogen enzyme preparation solution in water brought to desired p_H, 2 c.c. of $M/300$-xanthine solution at desired p_H and 2 c.c. of phosphate buffer ($M/3$) used.

	Oxygen absorption in c.c. at p_H				
Time.	5·2	6·2	7·1	8·0	9·1
15 min.	0·0157	0·0248	0·0388	0·0482	0·0423
30	0·0216	0·0362	0·0469	0·0603	0·050
60	0·0216	0·0392	0·050	0·0661	0·0560

TABLE I*b*.

Substrate—salicylaldehyde. 4 C.c. of 3% enzyme solution, 2 c.c. of *M*/100-salicylaldehyde at desired p_H and 2 c c. of phosphate buffer used.

	Oxygen absorption in c. c. at p_H				
Time.	5·2	6·2	7·1	8·0	9·1
15 min.	0·010	0·010	0·0212	0·0241	0·0267
30	0·0143	0·0162	0·0299	0·0372	0·0362
60	0·0162	0·0196	0·0352	0·0421	0·0412

TABLE I*c*.

Substrate—acetaldehyde. 4 C.c. of enzyme solution, 2 c.c. of *M*/5-acetaldehyde at desired p_H and 2 c c. of phosphate buffer used.

	Oxygen absorption in c. c. at p_H				
Time	5·2	6·2	7·1	8·0	9·1
15 min.	0·0072	0·020	0·0231	0·0311	0·0298
30	0·0126	0·0271	0·0312	0·0412	0·0401
60	0·0126	0·0312	0·0346	0·0445	0·0445

Thus the optimum p_H for the action of milk dehydrogenase using xanthine, salicylaldehyde and acetaldehyde as substrates and molecular oxygen as hydrogen acceptor, has been found to be 8·0. With methylene blue as hydrogen acceptor, Wieland and Rosenfeld obtained p_H 8 as the optimum p_H for the oxidation of xanthine and salicylaldehyde, while Dixon and Thurlow with methylene blue and hypoxanthine found that the reaction velocity was not affected between p_H 5·5 and 9.

Optimum Substrate Concentration.—Using xanthine, salicylaldehyde and acetaldehyde at opimum p_H (*i.e.*, p_H 8·0) with the same concentration of the enzyme solution and phosphate buffer, the following variation of oxygen uptake was noted with the variation of substrate concentration.

TABLE II*a*.

Substrate—xanthine. 4 C.c. of 3% enzyme solution at p_H 8·0, 2 c.c. of substrate at p_H 8·0 and 2 c.c. of phosphate buffer used.

	Oxygen uptake with substrate conc. of			
Time.	*M*/400.	*M*/800.	*M*/1200.	*M*/1600.
15 min.	0·0147 c.c.	0·0157 c.c.	0·0514 c.c.	0·0405 c.c.
30	0·0249	0·0264	0·0642	0·050
60	0·0264	0·0302	0·0690	0·0535

TABLE II*b*

Substrate—salicylaldehyde. 4 C.c. of 3% enzyme solution at p_H 8·0; 2 c.c. of substrate at p_H 8·0 and 2 c.c. of phosphate buffer used.

	Oxygen uptake with substrate conc. of			
Time.	*M*/100.	*M*/200.	*M*/400.	*M*/600.
15 min.	0·010 c.c.	0·0172 c.c.	0·0256 c.c.	0·0251 c.c.
30	0·0162	0·020	0·0360	0·0351
60	0·0219	0·0236	0·0402	0·0382

TABLE II*c*.

Substrate—acetaldehyde. 4 C.c. of 3% enzyme solution at p_H 8·0; 2 c.c. of substrate at p_H 8·0 and 2 c.c. of phosphate buffer used.

	Oxygen uptake with substrate conc. of			
Time.	*M*/6.	*M*/10.	*M*/20.	*M*/30.
15 min	0·0092 c.c.	0·0132 c.c.	0·030 c.c.	0·0210 c.c.
30	0·0176	0·020	0·0395	0·0331
60	0·020	0·023	0·0436	0·0360

It will be evident from the above that the optimum p_H and using 4 c.c. of 3% enzyme solution at requisite p_H in a total volume of 8 c.c. of the reaction mixture, the followings are the optimum substrate concentrations.

Xanthine, *M*/1200; salicylaldehyde, *M*/400; acetaldehyde, *M*/20.

Experiments with Dyestuffs.

The effect of the dyestuffs on the oxidation of the substrates, xanthine, salicylaldehyde, and acetaldehyde was observed under optimum conditions. The method was to determine the amount of oxygen absorbed in certain periods by the enzyme, the substrate, and buffer under optimum conditions and the same by the substrate, buffer and the enzyme which has already been subjected to the action of various dyestuffs for half an hour. Comparing the absorption of oxygen in both cases, the amount of inhibition produced by the dyestuffs could be calculated.

In the case of the action of the dyestuffs, 4 c.c. of 3% enzyme solution at p_H 8·0, 1 c.c. of *M*/3-phosphate buffer and 1 c.c. of 1/750-dye solution were placed in the Barcroft vessel. The concentration of the dye in the vessel was now 1/4500. The vessel was then allowed to stay for ½ hour in the thermostat at 37° so as to subject the enzyme to the action of dyestuff. After this period 2 c.c. of the substrate at optimum concentration and previously brought to p_H 8·0 and to 37°, were added quickly to the vessel and thus the volume was made up to 8 c.c. The concentration of the dye was now 1/6000 in the reaction mixture. The vessel was then shaken. Duplicate estimations were carried out in every case and the mean results were taken.

The action of a large number of acidic and basic dyestuffs from different series, *e.g.*, triphenylmethane, monoazo, tetraazo, diphenylmethane, pyronine, thiazine, safranines, the eurhodines and also hæmatoxylin were tried. The results obtained are summarised in the following table.

TABLE III.

Mean percentage of inhibition.

Acidic Dyestuffs.				Basic Dyestuffs.			
	Xanthine.	Acetaldehyde.	Salicylaldehyde.		Xanthine.	Acetaldehyde.	Salicylaldehyde.
Hæmotoxylin	Nil	Nil	Nil	Janus green	26·6	21·2	19·2
Erythrosin	39·5	41·9	39·4	Ethyl violet	62	54·1	48·3
Soluble blue	2	Nil	Nil	Methyl violet	22·9	21·9	11·9
Eosin yellow	Nil	Nil	Nil	Methylene violet	20·1	21·6	18.4
Eosin bluish	2·7	Nil	5·2	Gentian violet	38·9	29·9	21·2
Acid green	Nil	Nil	Nil	Crystal violet	27	55·7	46·8
Orange-G.	22·3	20·9	22·2	Bismarck brown	62·5	60	57·4
Neutral red	Nil	4·7	6·9	Safranine	34·2	21·5	22·1
Congo red	Nil	1·9	5·2	Pyronine	Nil	1·9	Nil
Benzopurpurine	1·5	2·7	Nil	Auramin	34·9	37·9	38·2
Water blue	Nil	3·9	Nil	Toluidine blue	73·8	75·7	75.8
Acid fuchsin	1·5	Nil	Nil	Brilliant green	9·1	6·7	6·8
				Chrysoidine	Nil	2·0	Nil
				Malachite green	17·4	14·3	15·9

It will be seen from the above results that all the dyestuffs behave exactly similar towards xanthine and aldehyde oxidation by the milk enzyme. Considering the results as a whole, the acidic dyestuffs with the exception of erythroisn and orange-G, are without any effect on the oxidation of the xanthine and the aldehydes and the two acidic dyestuffs, erythrosin, and orange-G, inhibit both xanthine and aldehyde oxidation to the same extent. All the basic dyestuffs with the exception of pyronine and chrysoidine exert a pronounced and equal inhibitory effect on the oxidation of xanthine as well as of aldehydes. This action of all the dyestuffs, without any exception, make it almost certain that in milk, one and only one oxidising enzyme causes the oxidation of purine bases and aldehydes. The active group in the enzyme appears to be acidic in nature.

Experiments with Narcotics.

In order to see if narcotics and certain other substances affected the oxidation of purine bases and of the aldehydes in a different manner, the effect of four narcotics, *e.g.*, diethylurea, ethylurethane, phenylurethane and phenylurea, as well as of the following substances : *viz.*, pyrogallol, sodium hydrosulphite and gallic acid, was determined in a manner exactly similar to that for determining the effect of dyestuffs. The experimental results are given in the following table.

TABLE IV.

	Percentage inhibition.		
Substrates →	Xanthine.	Salicylaldehyde.	Acetaldehyde.
Narcotics.			
Diethylurea	1·9	2	3·8
Ethylurethane	1·7	0	0
Phenylurethane	1·6	5·6	5
Phenylurea	0	0	0
Other substances.			
Pyrogallol	24·1	20·1	26·3
Sodium hydrosulphite	1·9	3·9	1·2
Gallic acid	11·4	7	12·2

It will be found that the four narcotics are almost without any effect on the oxidation of xanthine as well as of the two aldehydes.

Similar results were obtained by Sen (*loc. cit.*). This observation runs contrary to the views of Keilin on oxidation who holds that narcotics have no action on the activity of the oxidisable system but inhibit the activity of the dehydrogenation system. Of the three substances pyrogallol, sodium hydrosulphite and gallic acid, pyrogallol has got a pronounced but same inhibitory effect on both oxidations. Sodium hydrosulphite is without any effect, while gallic acid exerts a slight inhibitory action on both the oxidations.

All these observations point to the identity of the Schardinger enzyme with the xanthine oxidase.

SUMMARY.

1. Using the caseinogen preparation of Dixon and Thurlow with air as the hydrogen accepter, the optimum p_H and the optimum substrate concentration of xanthine, salicylaldehyde and acetaldehyde oxidations have been determined.

2. The actions of various acidic and basic dyestuffs, from different series, on the oxidation of xanthine, salicylaldehyde and acetaldehyde by the milk enzyme, have been determined under optimum conditions.

3. It has been found that the acidic dyestuffs with the exception of erythrosin and orange-G are without any effect on the oxidation of the xanthine and the aldehydes. All the basic dyestuffs with the exception of pyronine and the chrysoidine exert a pronounced and equal inhibitory effect on the oxidation of xanthine as well as of aldehydes. The active group in the enzyme appears to be acidic.

4. The action of four narcotics and three other substances has been observed on the same oxidation systems and it has been found that the narcotics are without any effect on the oxidation of both purine base and aldehydes. Of the three other substances, pyrogallol has got a pronounced but same inhibitory effect on both oxidations. Sodium hydrosulphite is without any effect, while gallic acid exerts a slight inhibitory action on both the oxidations.

5. All these observations point to the identity of the Schardinger enzyme with the xanthine oxidase.

Our thanks are due to Prof. J. C. Ghosh for his interest in our work.

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Electronic Theory of Valency and the Constitution of Aromatic Diazo Compounds.

By Pulin Bihari Sarkar.

Though the diazo compounds were discovered in 1858 by Peter Griess and the utility of these in synthetic organic chemistry and in the chemistry of dyestuffs have been thoroughly exploited, the problem regarding their constitution still remains an open one.

It is needless to recall the details of controversy or the many mistakes and retractions made on both sides of the rival schools of thought.

Stereoisomerism was all along advocated by Hantzsch and his pupils whilst the structural isomerism was upheld by no less authorities than Blomstrand, Jacobson, V-Meyer, von Pechmann and Bamberger. Universal agreement has been reached by both the schools regarding the diazonium compounds. Blomstrand's formula $\begin{matrix}\phi\\ X\end{matrix}\!\!>\!N\equiv N$ being accepted and that of Kekulé, *viz.*, $\phi-N=N-X$ being rejected (where ϕ stands for benzene nucleus and X for strong electro-negative elements like the halogens).

The bone of contention is the explanation of the isomeric diazo compounds.

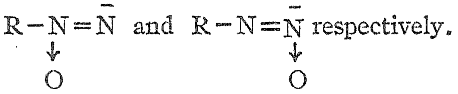
Defects of Hantzsch's Views.

(*i*) Stereoisomers, in general, resemble one another very closely in chemical properties, whereas the *syn*- and *anti*-compounds of Hantzsch differ very markedly.

(*ii*) Close resemblance of *syn* with diazonium compounds, their instability and explosive character, led Hantzsch to assume that in many cases, *syn* behaves as a pseudo-diazonium—equilibrium exists between them not only in solution but solid solutions of the two are frequent.

(*iii*) The difference in the absorption spectra of *syn*- and *anti*-diazotates of potassium.

Angeli from his studies of isomeric unsymmetrical azoxy compounds, came to the conclusion that the *normal* and *iso*-diazotates are structural isomers, the corresponding ions having the formulæ



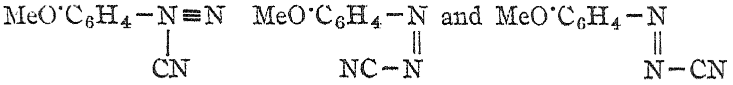
$$R-\underset{\substack{\downarrow\\ O}}{N}=\overset{-}{N} \text{ and } R-N=\underset{\substack{\downarrow\\ O}}{\overset{-}{N}} \text{ respectively.}$$

(*iv*) According to the rival school, Hantzsch has not been able to prove satisfactorily that the isomeric non-electrolytic diazo-cyanides as well as the diazo-sulphonates are true stereoisomers, cyanides and sulphites themselves having tautomeric structures.

Defects of the Structural Formula so far advocated.

(*i*) The main and the gravest objection is that the normal diazotate of potassium is formulated exactly as the diazonium hydroxide, whence it follows that once we are to assume diazonium hydroxide as a strong base and again as a weak acid.

(*ii*) Existence of the three isomeric diazo-cyanides from *p*-anisidine obtained by Hantzsch, namely,



$$MeO{\cdot}C_6H_4-\underset{\substack{|\\ CN}}{N}\equiv N \quad MeO{\cdot}C_6H_4-\underset{\substack{\|\\ NC-N}}{N} \text{ and } MeO{\cdot}C_6H_4-\underset{\substack{\|\\ N-CN}}{N}$$

Colourless soluble electrolyte.

Labile coloured non-electrolyte.

Stable coloured non-electrolyte.

was regarded by Hantzsch himself and his supporters as a very strong proof of his stereochemical theory since Bamberger's structural theory could only account for two of them.

A critical examination of the theories so far put forward reveals that

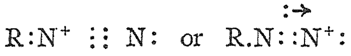
(*a*) In diazonium salts there is a triple bond between two N atoms, one being pentavalent and the other trivalent.

(*b*) In diazo compounds regarding the accepted Hantzsch-Kekulé formula, there is a double bond between the two N atoms, both being tervalent.

Modern Electronic Theory of Valency and its Deductions.

It predicts all the cases of isomerism hitherto observed for example, in diazonium compounds, which are electrolytes, the only formula admissible is $R—N^{+}_{2}\,|\,\overline{X}$

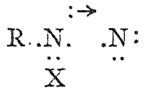
The octet theory gives the possible structures of RN^{+}_{2}-ion according as the electron taken up by X comes from the one or the other of the N atom as given below :



$$R{:}N^{+}\;\vdots\vdots\;N{:}\quad\text{or}\quad R.N\overset{:\rightarrow}{:}{:}N^{+}{:}$$

Both are non-distinguishable from one another and thus isomerism is precluded.

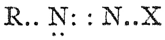
In diazo compounds, however, isomerism is possible according as X is attached to one or other of the N atom leading to the formation of non-electrolytes as given below.



$$\begin{array}{l} R..\overset{:\rightarrow}{\underset{\cdot\cdot}{N}.}\quad .\underset{\cdot\cdot}{N}{:} \\ \quad\; X \end{array}$$

(the so-called *syn* of Hantzsch)

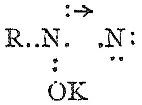
and



$$R..\underset{\cdot\cdot}{N}{:}\,{:}\,\overset{\cdot\cdot}{N}..X$$

(the so-called *anti*—of Hantzsch)

We believe Bamberger would have been correct had he given the formula for *syn*-diazotate of potassium (lablile,—normal) as



$$\begin{array}{l} R..\overset{:\rightarrow}{N.}\quad .\underset{\cdot\cdot}{N}{:} \\ \quad\;\; \vdots \\ \quad\; \dot{O}K \end{array}$$

This, of course, we cannot expect near about 1900, for translated into the then classical valency formula one nitrogen would be tetrad and the other diad.

We consider that Hantzsch's stereochemical idea is not at all necessary to explain the isomerism of *normal* and *iso*diazotates of potassium.

One noteworthy point is that the electronic theory of valency leads to formulation which is really a compromise between the two rival schools. It supports Hantzsch's views so far as it concerns the double bond between two N atoms; on the other hand, it supports Bamberger's views so far as it concerns the pentavalency of the N atom linked with R in the case of *syn*-diazo compounds. It also supports Angeli's views.

We think this is the main reason why "*syn*" and diazonium compounds resemble one another so much.

The very disproportionate (unequal) sharing of electrons between two N atoms is the real cause of the instability of "*syn*" compounds.

We consider that the structural formulæ based on electronic theory of valency as advocated in this paper can meet with all the objections raised by Hantzsch against structural theory.

Electronic theory can predict the following cases :

(*i*) When X is strongly electronegative and when the electropositivity of the $C_6H_5N_2$-group is augmented by the substitution of Me or OMe in the *ortho*-position of the benzene nucleus, only diazonium compounds will be formed.

(*ii*) When X is weakly electronegative or when the electropositivity of $C_6H_5N_2$-group is diminished by the substitution of Br, NO_2, etc., in the *ortho* or *para*-position of the benzene nucleus, diazo compounds will result.

Hantzsch assumes that the "normal salts with strong (mineral) acids are in the solid state, mainly diazonium but partly (especially the halides) solid solutions of diazonium and *syn*-diazo ; in solution they give almost entirely the diazonium ions. These can now be better explained by the deformation theory of Fajans and on the idea of easy conversion of co-valent "syn" compounds to electrovalent diazonium compounds.

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Available Nitrogen in Tropical Soils. Part I.

By N. R. Dhar and S.K. Mukherji.

Regarding the amounts of available nitrogen (sum of ammoniacal and nitric nitrogen) present in English soils, Russell, ("Soil Conditions and Plant Growth," 1932, pp. 237, 475) has stated as follows:—

"In normal conditions, the nitrate and ammonia together rarely account for more than one per cent. of the nitrogen in the soil."

"Usually the total amount of nitrogen is so large in comparison with the amount of nitrate that the changes in amount fall within the limits of experimental error."

"Neither ammonia nor nitrate normally occurs in the soil in any great quantity; a usual range on land carrying vegetation is from 5 to 25 parts of nitric nitrogen and about 5 to 10 parts of ammonia per million of soil, corresponding to about one to three per cent. of the total nitrogen."

The amount of available nitrogen in Russian soils varies from 0·36 to 4·6%.

In foregoing publications (*cf.* Dhar, "Influence of Light on Some Biochemical Processes," 1935), it has been emphasised that the oxidation processes taking place in the soil are facilitated to a greater extent in tropical countries due to sunlight and higher soil temperatures than in temperate climates. It is expected, therefore, that the percentage of available nitrogen in the tropical soil is greater than in cold countries.

In order to test this point, we have determined the total, ammoniacal and nitric nitrogen of samples of soils collected from different parts of India. Our results can be summarised as follows:—

Assam (Nyagora tea estate). Four samples of soil analysed; the available nitrogen varies from 25·1 to 40·4% of the total nitrogen, of which the variation is from 0·092 to 0·139 % of the soil.

Bengal (Dacca and Nadia). Six samples analysed; the available nitrogen varies from 14·3 to 29·7% of the total nitrogen, of which the variation is from 0·057 to 0·227 % of the soil.

Bihar (Pusa). Five samples collected in July 1932 and analysed in April 1935; the available nitrogen varies from 28·1 to 47·7% of the total nitrogen, of which the variation is from 0·0238 to 0·0313 % of the soil.

United Provinces (Allahabad). (*a*) Thirteen samples of ordinary garden soil analysed ; the available nitrogen varies from 10 to 31·6% of the total nitrogen, of which the variation is from 0·0347 to 0·0582% of the soil.

(*b*) Five samples of molassed soil of which the C: N ratio is constant, analysed ; the available nitrogen varies from 11·7 to 28% of the total nitrogen, of which the variation is from 0·0437 to 0·09% of the soil.

The Punjab.—(Ranjitkot, Hiyatpur and Chhanwali). Three samples analysed ; the available nitrogen varies from 13·4 to 15·2% of the total nitrogen, of which the variation is from 0·04 to 0·0582 % of the soil.

Madras (Waltair). Two samples analysed ; the available nitrogen varies from 15 to 24·9% of the total nitrogen, of which the variation is 0·0309 to 0·0625% of the soil.

The foregoing results show that the amounts of available nitrogen varies from 10 to 47·7% of the total nitrogen in the soils collected from different parts of India. The percentage of available nitrogen of a soil from Bangalore, which is a cool place is 8·5. Hence the portion of available nitrogen in comparison with the total nitrogen in tropical soils is much greater than that present in soils of temperate climates. It appears, therefore, that the solar radiations, which fall on the tropical soil, help in the oxidation of the nitrogenous substances present in the soil, which is rendered suitable for plant growth, although the total nitrogen in tropical soils is generally less than in those of temperate countries.

SUMMARY.

1. Experiments show that the available nitrogen in soils collected from Assam, Bengal, Bihar, United Provinces, the Punjab, and Madras, varies from 10 to 47·7% of the total nitrogen. In English soils, this value is 1% and in Russian soils, it is 0·36 to 4·6%. Hence the available nitrogen in tropical soils is greater than in the soils of temperate climates.

2. It seems that the solar radiations falling on the tropical soil help in the oxidation of the nitrogenous compounds to ammonia and nitrate, which are available for the plants, although the total nitrogen is less in tropical soils than in those of cold countries.

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Interaction of Sulphur Dichloride with Substances Containing the Reactive Methylene Group.

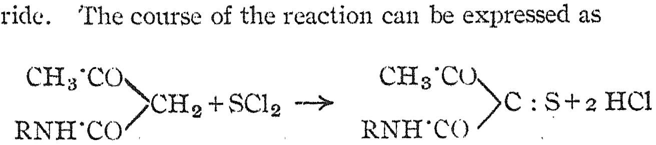
Part II.

By K. G. Naik and S. A. Vaishnav.

During previous investigations with sulphur dichloride, it was observed that it reacts with substances containing the reactive methylene group, giving rise to products containing the grouping -SCl (Naik and Jadhav, *J. Indian Chem. Soc.*, 1926, **3**, 260).

When sulphur dichloride was made to react with the substances, enumerated in the table at the end, under the same conditions as used by Naik and Jadhav, a gummy mass was obtained which was very difficult to work up. When attempts were made to purify these products by repeated purifications in mixed solvents, the original amide was obtained, showing that the reaction product, if at all formed, was decomposed during subsequent treatment.

It is well known that acetoacetic ester and its derivatives are in general more reactive than malonic ester and its corresponding derivatives, and therefore, it was thought advisable to modify the experimental conditions allowing a lower temperature for the reaction than that used by Naik and Jadhav. Pure dry benzene was selected as the solvent in the present work as it does not react with sulphur dichloride. The course of the reaction can be expressed as



$$\begin{matrix} CH_3\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>\!CH_2 + SCl_2 \rightarrow \begin{matrix} CH_3\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>\!C:S + 2\,HCl$$

The compound was precipitated very slowly, the precipitation appearing to be complete on the following day, though in some cases, the reaction mixture had to be kept for two days. To avoid the formation of a paste all precautions to exclude moisture had to be taken and the excess of sulphur dichloride was removed by several washings with dry benzene and dry petroleum.

The following considerations led us to assign the constitution given to these compounds.

(*i*) When the sulphide of acetoacet-β-naphthylamide is hydrolysed with caustic potash, β-naphthylamine is obtained.

(*ii*) The reduction by alkaline hydrosulphide gives back the original amide.

EXPERIMENTAL.

Interaction of Sulphur Dichloride with Acetoacetanilide.—The amide (3·6 g., 1 mol.) was suspended in dry benzene (25 c. c.) in a conical flask and sulphur dichloride (3 g., 1·1 mol.) was added. The flask was immediately corked tightly with a calcium chloride tube.

The reaction started vigorously and copious fumes of hydrochloric acid were evolved and the amide went into solution. The reaction subsided after a few minutes and then slow evolution of fumes continued. After 3 hours extremely slow precipitation began, which was completed on the next day. It was then filtered and washed free from the dichloride with dry benzene and petroleum when it separated as minute silky crystals, m.p. 196-97°. The compound is sparingly soluble in benzene and alcohol and insoluble in carbon disulphide and petroleum. (Found : N, 6·96 ; S, 15·76. $C_{10}H_9O_2NS$ requires N, 6·72 ; S, 15·47 per cent).

Hydrolysis of Acetoacet-β-naphylamide Sulphide.—5 G. of the compound were added to a solution of caustic potash (3 g.) in a small quantity of water and the whole was refluxed for 2 hours. The mixture was then cooled and filtered and the precipitate was washed with cold water till the filtrate was free from alkali. The solid, on recrystallising from hot water, gave rosy crystals, m. p. 110° (mixed m. p. with β-naphthylamine).

The solid residue, obtained on evaporating the filtrate to dryness , was treated with hydrochloric acid when hydrogen sulphide was found to evolve.

Reduction of Acetoacet-β-naphthylamide Sulphide by means of Alkaline Hydrosulpide.—5 G. of the compound were put into 50 c. c. of alcohol and refluxed for about an hour. An aqueous solution of sodium hydrosulphide (prepared by saturating 1·5 g. of caustic soda with hydrogen sulphide in a small quantity of water), and caustic soda (5·7 g. in a small quantity of water) was gradually added to it. The brown solution on dilution gave a precipitate, which was filtered and washed free from alkali and crystallised from benzene and petroleum, m. p. 103°. It was thus found to be the original amide.

The other compounds were prepared in the same way and the following table summarises the properties of the compounds obtained from the amides.

Amides.	M.p.	Properties.	Formulæ.	Analysis.	
				Found.	Calc.
Acetoacetanilide	196°	Silky needles	$C_{10}H_9O_2NS$	S, 15·76 N, 6·96	15·47 6·72
Acetoacet-*o*-toluidide	184°	Tuft-like crystals	$C_{11}H_{11}O_2NS$	S, 14 57 N, 6·57	14·48 6·34
Acetoacet-*p*-toluidide	130°	...	$C_{11}H_{11}O_2NS$	S, 14·79	14·48
Acetoacet-α-naphthyl-amide	184°	Needle-shaped crystals	$C_{14}H_{11}O_2NS$	12·70	12·45
Acetoacet-β-naphthyl amide	179°	Soft small needles	$C_{14}H_{11}O_2NS$	12·74	12·45
Acetoacetxylidide (1 :4 :5)	209°	Amorphous	$C_{12}H_{13}O_2NS$	13·94	13 61
Acetoacetxylidide (1 :3 :4)	201°	...	$C_{12}H_{13}O_2NS$	14·06	13·61

The authors desire to record their thanks to the Government of His Highness the Maharaja Gaekwar of Baroda for a grant which has defrayed the expenses incurred during this research.

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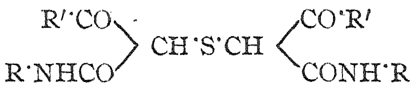
Interaction of Thionyl Chloride with Substances Containing the Reactive Methylene Group. Part V.

By K. G. Naik and S. A. Vaishnav.

A study of the interaction of thionyl chloride on substances containing the reactive methylene group (Naik and Parekh, *J. Indian Chem. Soc.*, 1930, **7**, 137) showed that sulphoxides of the general formula $R\cdot NH\cdot CO\cdot C : SO\cdot CO\cdot NHR$ are formed, which by the further reducing action of thionyl chloride condense to form sulphides, $[(R\cdot NHCO)_2C : S : C\ (R\cdot NHCO)_2]$. Naik and Thosar (*ibid.*, 1932, **9**, 127) investigated this reaction further and obtained sulphides of the type



$$\begin{matrix} R'\cdot CO \\ R\cdot NHCO \end{matrix}\!\!>CH\cdot S\cdot CH<\!\!\begin{matrix} CO\cdot R' \\ CONH\cdot R \end{matrix}$$

from the substituted amides of malonic acid and acetoacetic acid, and sulphides of the type $CONHR\cdot C : S\cdot COOC_2H_5$ from the amates of these acids.

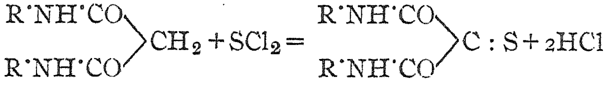
It was observed during these investigations that the presence of foreign substances in the reaction mixture affected the course of the reaction to a very great extent. It was, therefore, thought interesting to examine the effects of catalysts on this reaction and in the present work finely divided copper was used as a catalyst.

When copper was used as a catalyst in the interaction between thionyl chloride and malondiphenylamide, the following substance was obtained : $(C_6H_5\ NH\cdot CO)_2\ C : S$.

Michaelis and Philips (*Ber.*, 1890, **23**, 559), who obtained a sulphide by the action of thionyl chloride on acetoacetic ester, assumed that thionyl chloride behaves as if it were a mixture of sulphur dichloride and sulphuryl chloride.

We do not find support for this view of the reaction because if sulphuryl chloride is formed, it would, in all probability, have acted on some of the amide and given rise to chloro-compounds (*cf.* Naik and Shah, *J. Indian Chem. Soc.*, 1927, **4**, 11). In all probability the thionyl chloride decomposes in presence of copper into SCl_2, SO_2 and copper chloride (as with other metals, *vide* Mellor, 'Comprehensive

Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 662). This view finds further support in the fact that when the used-up catalyst is lixiviated with water, a green solution, showing the presence of copper chloride, is obtained and that sulphur dioxide can be detected in the gaseous products of the reaction. The reaction may be represented thus :—



$$\left.\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CO}\\ \mathrm{R{\cdot}NH{\cdot}CO}\end{array}\right\rangle CH_2 + SCl_2 = \left.\begin{array}{l}\mathrm{R{\cdot}NH{\cdot}CO}\\ \mathrm{R{\cdot}NH{\cdot}CO}\end{array}\right\rangle C : S + 2HCl$$

The above constitution has been assigned to these compounds from the following considerations :—

(*i*) Acetoacetic ester, which does not contain a phenyl group, reacts with thionyl chloride to form a sulphide which shows that the hydrogen atoms attacked are those of the reactive methylene group and neither those of the phenyl group nor those of the -NHR group (Michaelis and Philips, *loc. cit.*).

(*ii*) On reduction with alkaline hydrosulphide, the original amide is obtained.

EXPERIMENTAL.

Interaction of Malondiphenylamide with Thionyl Chloride.—Thionyl chloride (2·5 g.) was added to malondiphenylamide (2·5 g) in dry benzene (30 c.c.) containing copper powder (1 g.). Gases were evolved and soon the mixture turned red. After ½ hour the mixture was heated under reflux for 4 hours, filtered hot and the cold solution dropped slowly into a large amount of dry petroleum with constant stirring. A compound was precipitated which was reprecipitated from benzene and petroleum 3 or 4 times, m.p. 105-6°, with previous shrinking at 80°. It is soluble in benzene, slightly so in carbon disulphide and insoluble in petroleum. (Found : N, 9·58; S, 11·41. $C_{15}H_{12}O_2N_2S$ requires N, 9·85 ; S, 11·26 per cent).

Hydrolysis with Water.—The above compound (2 g.) was heated with 20 c c. of distilled water for 30 minutes. The paste formed was taken out and the water filtered off hot, when on cooling a crystalline substance was obtained. This was collected and recrystallised from alcohol and was found to be the original amide, m.p. 225-26°. The paste was treated with carbon disulphide and on evaporation of the disulphide, free sulphur was left behind.

Reduction by Alkaline Hydrosulphide.—The substance (5 g.) was refluxed for about an hour with 50 c.c. of alcohol. An aqueous solution of sodium hydrosulphide (prepared by saturating 1·5 g. of caustic soda with hydrogen sulphide in a small quantity of water) and caustic soda (5·7 g. dissolved in a small quantity of water) was gradually added to it, when a brown solution was obtained, which was diluted with a large quantity of water when precipitation occurred. The precipitate was collected and washed free from alkali by hot water and crystallised from alcohol, m.p. 224-25°. It was malonanilide.

Hydrolysis by Caustic Potash.—The compound (5 g.) was refluxed for 2 hours with a solution of caustic potash (10 g. in 16 c.c. of water) and the cold solution diluted with water and extracted with ether. On evaporating the ether the oily liquid was found to be aniline. The residue was treated with hydrochloric acid, when hydrogen sulphide was found to evolve.

The other compounds were prepared in the same way and the following table summarises the properties of the compounds obtained from the different amides.

Amides.	M. p.	Shrinks at.	Formulæ.	Analysis. Found.	 Calc.
Malondiphenylamide	105°	80°	$C_{15}H_{12}O_2N_2S$	S, 11·41 N, 9·58	11·26 9·85
Malondi-*o*-tolylamide	138°	110°	$C_{17}H_{16}O_2N_2S$	S, 10·63	10·25
Malondi-*p*-tolylamide	108°	60°	$C_{17}H_{16}O_2N_2S$	S, 10·30 N, 8·76	10·25 8·97
Malondi-*m*-tolylamide	114°	60°	$C_{17}H_{16}O_2N_2S$	S, 10·33	10·25
Malondi-*α*-naphthylamide	168°		$C_{23}H_{16}O_2N_2S$	8·83	8·33
Malondixylidide (1:3:4)	126°	95°	$C_{19}H_{20}O_2N_2S$	9·03	9·41
Malondixylidide (1:4:5)	146°	100°	$C_{19}H_{20}O_2N_2S$	9·21	9·41

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Halogenation. Part XIII. Bromination and Iodination of Some Halogenated Benzenes.

By Phuldeo Sahai Varma and S. Shankarnarayanan.

A survey of the literature shows the lack of any systematic study of the direct action of bromine and iodine on partially halogenated benzenes. The bromo and iodo derivatives, which have been prepared before, have generally been done by indirect methods, by replacing the amino group by the halogens. The compounds treated in this paper are *p*-dichlorobenzene, bromo- and *p*-dibromobenzenes and iodobenzene. Direct bromination and iodination of bromobenzene have not been carried out before though the products mentioned here have been obtained by other methods. In the case of *p*-dichlorobenzene, however, 2 : 5-dichloro-1 : 4-dibromobenzene and 3 : 6-dichloro-1 : 2 : 4 : 5-tetrabromobenzene have been prepared before by heating the compound with excess of bromine in presence of iron or $AlCl_3$ respectively (Wheeler and Mac Farland, *Amer Chem. J.*, 1897, **19**, 366 ; Mouneyrat and Pouret, *Compt. rend.*, 1899, **129**, 1607).

Attempts have been made in this paper to bring about direct bromination and iodination in presence of the following substances : (*i*) concentrated or fuming nitric acid, (*ii*) concentrated or fuming sulphuric acid, (*iii*) a mixture of concentrated sulphuric and nitric acids, or fuming sulphuric and nitric acids, (*iv*) sodium nitrite and fuming sulphuric acid, and (*v*) nitrosulphonic acid mixture. The methods adopted are similar to those used in this laboratory for the preparation of the mixed halogen derivatives of toluene and xylene (Varma and others, *J. Indian Chem. Soc.*, 1934, **11**, 293 ; 1935, **12**, 245).

The experiments carried out with bromo-, dibromo- and iodobenzenes have given satisfactory results. Bromobenzene on bromination gave *p*-dibromo and 1 : 2 : 4 : 5-tetrabromobenzenes and on iodination 4-bromo-1-iodobenzene gave 4-bromo-1-iodobenzene and 2 : 5-diiodobenzene. The best yields of the above compounds have been obtained in presence of (*a*) sodium nitrite and fuming sulphuric acid and (*b*) nitrosulphonic acid mixture. *p*-Dibromobenzene gave 2 : 5-dibromo-1-iodobenzene with some difficulty.

With *p*-dichlorobenzene it has been possible to obtain the dibromo derivative only. In no case is the monobromo derivative obtainable. An attempt was made to sulphonate the *p*-dichlorobenzene first and then to replace the sulphonic acid group by a bromine atom, but even that proved unsuccessful (*vide* replacement of sulphonic acid groups by nitro groups, Datta and Varma, *J. Amer. Chem. Soc.*, 1919, **41**, 2039; *J. Indian Chem. Soc.*, 1927, **4**, 321).

EXPERIMENTAL.

In the experiments, tabulated below, the initial compound and bromine were taken together in a round-bottomed flask and heated on a water-bath or a sand-bath under reflux condenser. The halogenating agent was added from the top of the condenser, 1 c. c. at a time at regular intervals. In the case of sodium nitrite and fuming sulphuric acid, sodium nitrite was taken in the flask along with other substances. When the whole mixture had been added, the heating was continued for a further period mentioned against each experiment, and in some cases left to stand for some hours or overnight. The contents were then washed several times with distilled water, and with dilute (1-2%) caustic soda solutions to remove the unreacted halogen. It was finally washed with water and the separated solid was filtered at the pump and recrystallised from a suitable solvent and the m p. determined. In each case the product was identified by m.p.

In the experiments on iodination, acetic acid was also taken in the flask, as it had been found that it aids iodination considerably. The most important results are summarised in the following table. From the results obtained it is apparent that under the experimental conditions described though the main product is *p*-dibromobenzene from monobromobenzene, a small (almost negligible) quantity of *o*-dibromobenzene is also obtained; but practically no *o*-diiodobenzene is formed on the iodination of monoiodobenzene.

Substance.	Halogen.	Halogenating agent.	Temperature and time.	Product and yield.
p-Dichlorobenzene (10 g.)	Bromine (8 c.c.)	$NaNO_2$ (12 g.) + fuming H_2SO_4 (15 c.c.)	200°, 4 hrs.	2 :5-Dichloro-1 :4-dibromobenzene (m.p. 146°), 4·0 g.
„	„	Nitrosulphonic acid (10 c.c.)	„ 6 hrs.	„ 4·5 g.
Bromobenzene (5 c.c.)	Bromine (8 c.c.)	$NaNO_2$ (3 g.) + fuming H_2SO_4 (3 c.c.)	Water-bath for 6 hrs.	p-Dibromobenzene (m.p. 89°) 3·4 g. (negligible quantity of *o*-dibromobenzene).
„	„	Nitrosulphonic acid (3 c.c.)	„ „	„
p-Dibromobenzene (5 g.)	„ (3 c.c.)	„ (2 c.c.)	200°, 4 hrs.	1 :2 :4 :5-Tetrabromobenzene (m.p. 180°), 1·3 g.
Iodobenzene (10 c.c.)	„ (5 c.c.)	„ (5 c.c.)	Water-bath for 4 hrs.	4-Bromo-1-iodobenzene (m.p. 91°) 4·5 g.
Bromobenzene (5 c.c.)	Iodine (10 g.) + acetic acid (10 c.c.)	„ (3 c.c.)	„ „	„ 4·8 g.
„	Iodine (20 g.) + acetic acid (10 c.c.)	$NaNO_2$(5 g.) + fuming H_2SO_4 (5 c.c.)	200°, 6 hrs.	„ 4·6 g.
p-Dibromobenzene (10 g.)	Iodine (25 g.) + acetic acid (20 c.c.)	Nitrosulphonic acid (10 c.c.)	200°, 42 hrs. and overnight.	2 :5-Dibrom-1-iodobenzene (m.p. 38°) 1·3 g.)
Iodobenzene (10 c.c.)	Iodine (10 g.) + acetic acid (10 c.c.)	$NaNO_2$ (10 g.) + fuming sulphuric acid (10 c c.)	200°, 4 hrs.	1 :4-Diiodobenzene (m.p. 129°), 7·2 g.
„	„	Nitrosulphonic acid (10 c.c.)	„	„ (9·8 g.)
Diiodobenzene (10 g.)	Iodine (20 g.) + acetic acid (20 c.c.)	Nitrosulphonic acid (15 c.c.)	200°, 6 hrs.	1 :2 :4-Triiodobenzene (m.p. 91°), 2·4 g.

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On the Proteinase in the Milky Juice of *Calotropis Gigantea*. Its Purification and Activation by Ascorbic Acid and Glutathione.

BY KALI PADA BASU AND MADHAB CHANDRA NATH.*

Basu and Nath (*J. Indian Chem. Soc. Sir P. C. Ray Comm. Vol.* 1933, p. 107) have already reported on the occurrence of a proteolytic enzyme in the milky juice of *Calotropis gigantea*. The enzyme, it was shown, could hydrolyse gelatine, casein, egg-albumin, and fibrin and its optimum p_H was 5·0. The juice was shown to contain a natural activator whose amount diminished as the plant grew older. Sulphuretted hydrogen, cysteine, and also hydrocyanic acid were found to exert an activating influence on the enzyme. The investigation has been continued with special reference to the purification and activation of the enzyme.

EXPERIMENTAL

The proteolytic activity was measured by titration with alcoholic potash solution from a micro-burette. Contrary to our previous result it has been found that the enzyme, both in presence of the natural activator as well as in presence of sulphuretted hydrogen, can hydrolyse peptone. Table I makes it clear.

TABLE I.

10 C.c. of 2% Witte peptone solution at p_H 5·0, 1 c.c. citrate buffer and the clear centrifugate from 1 c.c. juice, made up to 25 c.c. and 5 c.c. titrated. Temp. = 40°.

Activator	Hydrolysis (0·023 *N*-KOH).	
	After 1 hr.	After 3 hrs.
...	1·3 c.c	1·8 c.c.
H_2S	1·52	2·0

The juice was found to contain no dipeptidase and very little polypeptidase. In the milky juice of *Calotropis gigantea* only one enzyme, which appears to be very similar to papain, is responsible for hyrolysing the proteins to amino-acids. This observation is contrary to the view of Vines ("The Proteins of Plants," London, 1930) who holds that there are two proteases in plants *viz.*, (*i*) the peptase that hydrolyses protein molecules to peptones, and (*ii*) the ereptase that hydrolyses the peptones formed, to amino-acids, but supports the views of Willstäter (*Z. physikal. Chem.*, 1924, **138**, 184; 1926, **153**, 250).

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* Lady Tata Memorial Scholar.

Purification.

That the enzyme is present in the water soluble part of the juice is evident from Table II.

TABLE II.

Substrate—gelatine; 5 c.c. of 5% gelatine solution at p_H 5 ; 1 c.c. citrate buffer of p_H 5 ; Clear centrifugate from 1 c.c. juice made up to 25 c.c. and 5 c.c. titrated. Temp. 40°. (Sample of juice—B)

Hydrolysis (0·023N-KOH) after 1 hr.		
With 1 c.c. fresh juice.	With clear centrifugate from 1 c.c. juice.	With water insoluable portion from 1 c.c. juice.
1·33 c.c.	1·95 c.c.	0 c.c.

Attempts to purify the enzyme by precipitation of the aqueous solution with alcohol, lead acetate, or mercuric sulphate were not successful and resulted in the precipitation of inactive products. The residue obtained by treating the solid obtained by drying in juice in vacuum at the ordinary temperature with ether and acetone and also glycerine extract of the juice (dried in vacuum) were without any proteolytic activity.

In order to obtain the enzyme in a more active state, 100 c. c. of the juice were diluted with water and centrifuged. The clear liquid (650 c. c.) was divided into 5 fractions and each fraction treated in different manner.

(*a*) *First fraction.*—100 C. c. of the solution were made half saturated with ammonium sulphate, precipitate dialysed for 4 days in distilled water, later tested for proteolytic activity.

(*b*) *Second fraction.*—Filtrate from (*a*) was made full saturated with ammonium sulphate, precipitate dialysed and activity tested for.

(*c*) *Third fraction.*—100 C. c. were made 0·03 saturated with ammonium sulphate and dilute HCl was added, precipitate dialysed and activity studied.

(*d*) *Fourth fraction.*—100 C. c. of the solution were acidified with 2 c. c. of strong HCl, precipitate dialysed and proteolytic activity studied.

(*e*) *Fifth fraction.*—Activity was tested after simply dialysing 100 c. c. of the solution.

The following table shows the results.

TABLE III.

Substrate—gelatine. Activator-H_2S. $p_H = 5{\cdot}0$. Temp. = 40°.
Procedure same as in Table II.

Method of treatment.	Wt. of solid (equivalent to 1 c.c. juice).	Hydrolysis (0·023N-KOH) after	
		1 hr.	1 hr. per 0·1573 g. solid.
Centrifuged only	0·1573	2·35 c.c.	2·35 c.c.
(*a*) Centrifuged and half-saturated with ammonium sulphate and dialysed	0·0058	0·3	8·21
(*b*) Full saturated with ammonium sulphate and dialysed			
(*c*) 0·03 saturated with ammonium sulphate and acidified with HCl (dilute) and dialysed	0.0097 0·0056	0·9 Nil	14·58 Nil
(*d*) Acidified with HCl (strong) and dialysed	0·0041	Nil	Nil
(*e*) Dialysed after centrifuging	0·011	1·95	27·92

In determining the weight of solid equivalent to 1 c. c. juice, evaporations were, in all the above cases, done in vacuum at the ordinary temperature.

It will be evident from Table III that simple dialysis of the clear centrifugate from the juice yields the most active preparation. The precipitate obtained on half saturating the clear centrifugate with ammonium sulphate is only half as active as the precipitate obtained later on full saturation. The enzyme thus appears to be associated with a protein of the nature of albumin.

We have made a comparative study of the behaviour of calotropis proteinase and papain. The results obtained with fresh juice of both the plants are indicated in Table IV.

TABLE IV.

	Treatment.	Calotropis proteinase.	Papain.
(1)	Precipitation of the aq. extract with alcohol	Ppt. inactive	Ppt. active
(2)	Application of heat to the aq. extract	Not coagulable by heat	Coagulable at about 80°
(3)	(*a*) Half of the aq. extract saturation with am. sulphate	Ppt. active	No ppt.
	(*b*) Full saturation of the remaining mother-liq.	Do	Ppt. active
(4)	Effect of H-ion conc. on the solubility of the enzyme	Insoluble at *p*H lower than five and in dilute alkali	Same as in former

Activation.—It has previously been shown that reducing agents like HCN, H_2S and cysteine are capable of activating the enzyme, and that natural activators are present in the juice, specially of younger plants. The problem is to find out the nature of this natural activator. Ascorbic acid and glutathione are constituents of many plants and it would be interesting to see whether these two substances are present in the juice and whether they have got any activating action on the proteolytic enzyme present in the juice.

Gluthathione, ascorbic acid and cysteine in the juice were determined as follows. Titration with iodine solution (*cf.* Tunnicliffe, *Biochem. J.*, 1925, **19**, 194) gave the equivalent of all these three substances provided they were the only reducing substances present. The juice was then titrated with 2·6-dichlorophenol-indophenol according to the method of Birch, Harris and Ray (*Biochem. J.*, 1933, **27**, 580), Harris and Ray (*Biochem. J.*, 1933, **27**, 303). Another titration with 2:6-dichlorophenol-indophenol after removing cysteine as recommended by Emmerie (*Biochem. J.*, 1934, **28**, 268, 1153) gave the amounts of ascorbic acid and cysteine. Table V indicates the results.

TABLE V.

Titration with iodine soln.	Titration with 2 :6-dichlorphenol-indophenol.	Titration with the indicator after removal of cysteine with mercuric acetate
2 C.c. I_2 soln. containing 2·48 mg. I_2. Ω 9·10 c.c. of dil. juice. Ω 1·02 c.c. of original juice. Hence 1. c.c of juice Ω 2·432 mg. iodine.	5 C.c. of the indicator soln. Ω 0·595 mg. I_2. Ω 7·8 c.c. of dil. juice. Ω 0·874 c. c. of original juice. Hence ascorbic acid and cysteine in 1 c. c. juice Ω 0·68 mg. iodine.	1 C.c. indicator soln. Ω 3·5 c.c. of diluted juice. Ω 0·392 c.c. of original juice. Hence ascorbic acid in 1 c.c. juice Ω 0·304 mg. iodine.

Thus the calotropis juice contains per c.c. (if other reducing agents are assumed to be absent), 2·094 mg. glutathione, 0·211 mg. ascorbic acid and 0·180 mg. cysteine. An attempt was made to isolate the glutathione by the method of Hopkins (*J. Biochem.*, 1929, **84**, 269) but although a white cuprous salt was obtained with cuprous oxide we could ultimately isolate only oxalic acid.

The activating effect of ascorbic acid, ascorbic acid- Fe'' complex and of glutathione on the calotropis proteinase was then investigated. Parallel experiments were performed with papain as well. Two preparations of the latter were employed. In the first case the fresh juice from *Carica papaya* was extracted by standing overnight in the refrigerator with water. Secondly this aqueous extract was precipitated with alcohol. The calotropis enzyme was employed in the form of clear centrifugate of one c.c. juice. The results are shown in Table VI.

TABLE VI.

Substrate—gelatine. *p*H, 4·95. Temp. 40°. Procedure same as in Table II.

With clear centrifugate equivalent to 1 c.c. juice used.

	From *Calotropis gigantea*		From *Carica papaya.*		With solid papain (40 mg.)	
Activator.	Hydrolysis (in c.c. of ·023*N*-KOH) after					
	1 hr.	3 hrs.	1 hr.	3 hrs.	1 hr.	3 hrs.
...	0·60	0·70	1·75	2·50	1·05	1·30
H_2S	1·95	2·35	2·30	3·45	1·60	2·25
Glutathione (2·5 mg.)	1·90	2·40	2·20	3·30	1·85	2·35
Ascorbic acid (7 mg.)	1·75	1·85	2·05	3·10	0·90	1·15
Ascorbic acid (7 mg.) with $FeSO_4$ (20 mg.)	1·80	1·95	1·80	2·35	1·55	2·00

It will be seen from the Table VI that the aqueous extract of the enzyme from the fresh juice of *Calotropis gigantea* and *Carica papaya* behave very similar towards glutathione and ascorbic acid. Both glutathione and ascorbic acid act as activators and addition of ferrous iron does not increase the activating effect of ascorbic acid; indeed, in the case of juice from *Carica papaya*, iron seems to exert an inhibiting effect. The case is different with the solid preparation of papain obtained with alcohol. In this case ascorbic acid alone exerts no activating influence; it has on the other hand a slight retarding effect, but ascorbic acid together with iron acts as an activator. Similar result was obtained by Marchmann and Helmert (*Z. physiol. Chem.*, 1934, **223**, 127), who found that the gelatine-splitting power of Merck's papain was inhibited by ascorbic acid, but activated by ascorbic acid plus iron. Purr (*Biochem. J.*, 1935, **29**, 13), has recently observed that ascorbic acid alone cannot, but ascorbic acid-Fe$''$ complex can activate Merck's papain but neither can activate papain rendered inactive by hydrogen peroxide.

SUMMARY.

1. The proteinase in the milky juice of *Calotropis gigantea* which can hydrolyse gelatine, casein, fibrin, and egg-albumin (p_H optimum $=5$) can also hydrolyse peptone when activated.

2. The enzyme is soluble in water but treatment of the aqueous solution with alcohol, lead acetate or mercuric sulphate results in the formation of an inactive precipitate.

3. Both half-saturation and subsequent full saturation of the aqueous solution yield active precipitates, the latter being more active.

4. Simple dialysis of the solution results in the highest degree of purification of the enzyme.

5. Glutathione, ascorbic acid and cysteine appear to be present in the milky juice.

6. The enzyme in the clear centrifugate of the juice is activated by glutathione and by ascorbic acid. Ferrous iron does not increase the activating power of ascorbic acid. Similar results were obtained with aqueous extract of fresh *Carica papaya* juice.

7. Papain (obtained by precipitation with alcohol, from the fresh juice) is very slightly inhibited in its action by ascorbic acid but accelerated by ascorbic acid-Fe$''$ complex.

Our thanks are due to Prof. J. C. Ghosh for his interest in this investigation.

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A Method for the Estimation of Lead Volumetrically by Fajan's Method.

By Sachindra Nath Roy.

Wellings (*Analyst*, 1933, **58**, 331) suggested a method for the estimation of lead by titrating $Pb(NO_3)_2$ against standard caustic soda using fluorescein and its derivatives as adsorption indicator (*cf.* also *Analyst*, 1935, **60**, 316). In order to eliminate the difficulty of preparing standard caustic soda solution and to find out a more simplified method, attempts have been made to describe in this paper a volumetric method of estimation of lead, in which standard solutions of sodium carbonate have been employed instead of caustic soda using fluorescein as the adsorption indicator. The precipitated lead salt adsorbs lead ions at the equivalence point or just beyond (*i.e.*, with slight excess of lead ions) and the so-called 'lead body' thus formed adsorbs fluorescein ions from the solution with the formation of a brick-red lead fluorescinate on the surface of the precipitate. As the solubility of the precipitated lead salt is much below that of lead hydroxide, it appears that the present method will be much more precise than that suggested by Wellings (*loc. cit.*), though the colour change of the indicator is not so pronounced.

Acid solutions of lead should be evaporated to dryness on a water-bath ; the slight hydrolysis which might have taken place, will not vitiate the result, as the solubility product of the precipitated lead salt in an excess of carbonate ions is far below than that of the basic salt formed. The solution should not be neutralised with ammonia. The solid residue is then extracted with water and transferred to a conical flask, an excess of known volume of standard sodium carbonate is added to the solution, to which two or three drops of the indicator (0·2% solution of sodium fluorescinate) have been added. The solution is then titrated with standard solution of lead nitrate (the standardisation being effected by the same solution of sodium carbonate). The lead nitrate should be added (the reverse process is not so satisfactory) slowly and the solution well shaken continuously. The equivalence point is ascertained by the sudden disappearance of the greenish yellow tinge of fluorescein and simultaneous development of a yellowish-red colouration due to the formation of the dye-precipitate complex of pinkish colour on the surface of the precipitate. It is advisable to take the reading at the point at which further addition of one more drop of lead nitrate will give to the mixture, on shaking, an unmistakable yellowish-red tinge. In very dilute solutions (0·03N to 0·015N), the yellowish tinge is more prominent than the red and care should be taken during addition of the last few drops. A slight practice will enable the performer to find out the equivalence point with exactness.

The colour change is very delicate and titration results are accurate within 1% error even with 0·02N solutions. The concentration of indicator should, however, be consistent with that of the solution titrated. The best results are obtained with solutions of 0·05N strength.

It was noticed that the difference between the readings of lead sulphate obtained by the direct method and that estimated by the method described above vary from 0·0032 to 0·0040, the direct method giving the lower value, and is fairly constant between wide ranges of concentration, *e.g.*, 0·2 N to 0·015 N.

My grateful thanks are due to Prof. A. Maitra for his kindly suggesting this work and also for the interest he took in this invesigation.

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On the Measurement of Absolute Rates of Migration of Ions by the Method of Moving Boundaries. Part II.

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The ' moving boundary method ' can be utilised for the determination of the absolute rate of migration of an ion if the potential gradient under which the boundary moves can be accurately measured. Mukherjee's method (*Proc. Roy. Soc.*, 1923, **A 103**, 102) of measuring the cataphoretic speeds of colloidal particles is based on this principle. In a previous paper (Mukherjee, Mitra and Bhattacharyya, *J. Indian Chem. Soc.*, 1935, **12**, 177) a method of calculating the absolute rates of migration of both the 'leading' and the 'indicator' ions from known linear displacements of the boundary, moving under directly measured potential gradients, has been developed and applied in investigating rising ' anion boundaries ' between hydrochloric and picric acid solutions of approximately ' adjusted ' concentrations. The absolute rates of migration of the chloride ion were found to be distinctly lower than the accepted values at corresponding hydrochloric acid concentrations. In view of this and other interesting observations it was considered desirable to work in more detail with the hydrochloric acid—picric acid system.

The difficulties of reproducible measurements with boundaries between solutions of acids are well known (Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2741). In view of the high mobility of the hydrogen ion, disturbances arising from heating effects at an ' acid boundary ' are particularly troublesome. It was, therefore, considered desirable to compare the results obtained with the system (*a*) hydrochloric acid—picric acid, (*b*) sodium chloride—sodium picrate, (*c*) potassium chloride—potassium picrate. In very dilute solutions of sodium and potassium chlorides, the picrates were not so suitable as 'indicator' solutions owing to the difference in density between the two solutions forming the boundary being negligibly small. The much heavier iodeosin ion was found to be more convenient under such conditions. The iodeosin ion exhibits a strong red colour even at high dilutions and the boundary could be accurately located with a proper control of the colour of the back ground illumination. The iodeosin ion has been used as an indicator ion by Franklin and Cady (*J. Amer. Chem. Soc.*, 1904, **26**, 499) and by Longsworth (*J. Amer. Chem. Soc.*, 1930, **52**, 1897). Rising boundaries between potassium chloride and potassium salt of iodeosin have been investigated in this work.

The work of previous investigators (MacInnes and Longsworth, *Chem. Rev.*, 1932, **11**, 171) shows that the range of concentration adjustment of the 'indicator ion' which according to Kohlrausch (*Ann. physik*, 1897, **62**, 209) should be unlimited for a given concentration of the leading ion, is actually limited depending on the conditions of experiment. Results throwing light on the nature and mechanism of this concentration adjustment have been obtained. Some experimental observations recorded in the previous paper (Mukherjee and co-workers, *loc. cit.*) suggested a possible effect of the potential gradient in the upper liquid on the results though Kohlrausch's theory contemplates no such effect provided that the restoring effect of the current is strong enough to ensure a sharp boundary. Similar observations have been made by MacInnes and Smith (*J. Amer. Chem. Soc.*, 1923, **45**, 2246) and by Cady and Longsworth (*J. Amer. Chem. Soc.*, 1929, **51**, 1656) but no explanation of these observations have been given. The effect of the current has been followed in more detail in this work.

The influence of the area of cross-section of the measuring tube on the calculated rates of migration and particularly on the range of concentration adjustment has been studied. Boundaries between mixtures of electrolytes have been investigated. Using a measuring tube constructed from a standard micro-burette, the transference number of the chloride ion has been obtained from the volume swept by the boundary, and the current actually measured simultaneously with measurements of the linear displacement of the boundary. Further, knowing the potential gradients in the different layers, also the absolute rate of migration of the chloride ion has been calculated.

Theory and Method of Calculation.

(*a*) *Theory.*—The theory underlying the method has been discussed in detail in the previous paper. It will be helpful to reproduce it briefly as follows :

When a potential gradient acts across a boundary between a solution of hydrochloric acid and an equiconducting solution of picric acid such that the faster moving chloride ions are followed by the slower moving picrate ions, an automatic concentration adjustment in the picric acid takes place such that a more dilute solution of concentration c', governed by the relation $c/T=c'/T'$ comes out, c and c' denoting the concentrations and T and T', the transference numbers respectively of the chloride and the picrate ions. The concentration c remains unaltered.

Under steady conditions, the potential difference between two fixed planes at right angles to the direction of the current, one in the hydrochloric acid and the other in the picric acid solution, is given by

$$V=i[\sigma_1(x-x_1)+\sigma_2 x_1] \qquad \ldots \quad (i)$$

where i, is the constant current density employed; σ_1 and σ_2 are respectively the specific resistances of layers of hydrochloric and picric acid solutions; x_1 is the distance between the boundary and the fixed plane in picric acid and x is the total distance between the planes.

From equation (i)

$$\frac{\partial v}{\partial x}=i(\sigma_2-\sigma_1)=P \qquad \ldots \quad (ii)$$

and

$$\frac{\partial v}{\partial t}=i(\sigma_2-\sigma_1)\frac{\partial x}{\partial t}=i(\sigma_2-\sigma_1)\times \text{the velocity of the boundary}$$

$$=Q \quad \ldots \quad \ldots \quad \ldots \quad (iii)$$

P and Q are constants independent respectively of the position of the boundary and time.

Also the potential gradient in the picric acid layer is given as

$$i\sigma_2 = i\sigma_1+\frac{\partial v}{\partial x} \quad \ldots \quad \ldots \quad (iv)$$

It is possible to measure the potential gradients in both layers without measuring the cross-section of the tube if the potential gradient in the hydrochloric acid layer and $\partial v/\partial x$ are directly measured.

The above equations show that in absence of disturbing effects, *e.g.*, those arising from heating and diffusion, (*i*) the potential difference between the two planes should change linearly with time and also with the distance traversed by the boundary ; and (*ii*) this distance also should be linearly related with time.

(*b*) *Method of Calculation.* (1) *Rates of migration.*—The boundary being located between the side-limbs 2 and 3 (Mukherjee's apparatus: *cf.* previous paper) the difference in potential between two silver—silver chloride electrodes dipped into the side-limbs 1 and 2 is measured. Under satisfactory experimental conditions, this potential difference remains constant within ± 0·1 %. Knowing the effective distance between these side-limbs, the potential gradient in the leading solution can be calculated. As the boundary rises, the P. D. between side-limbs 2 and 3 increases chronologically. The increment corresponding to a given displacement of the boundary is measured, from which the increment per centimetre displacement ($\partial v/\partial x$) can be calculated ; on adding this increment to the constant potential gradient obtaining in the leading solution, the gradient in the 'indicator' electrolyte is obtained (*cf.* equation *iv*). By combining these gradients with the distance traversed by the boundary in a given interval of time, the absolute rates of migration of the 'leading' and also of the 'following' ions are obtained.

(2) *Transference numbers.*—The transference number of the 'leading ion' can be calculated with the aid of the equation $T = VcF/it$, where T denotes the transference number and c, the concentration of the 'leading ion' ; i, the constant current employed and t, the time during which the volume V has been swept by the boundary. For accurate determinations of the volume, the moving boundary apparatus was constructed from a standard micro-burette. The side-limbs 2 and 3 for potentiometric measurements were sealed too wide apart to vitiate the graduations over at least a distance of one centimetre midway between these side-limbs. The boundary was in all cases located in this region and the measurement discontinued when the boundary passed beyond it. The accuracy of the graduations of the tube was tested by a careful recalibration.

EXPERIMENTAL.

Excepting for a few modifications (*vide infra*) the experimental arrangements were similar to those employed in the previous paper

(Mukherjee and co-workers, *loc. cit.*). Rising boundaries between solutions of different concentrations of (1) hydrochloric acid and picric acid, (2) sodium chloride and sodium picrate, (3) potassium chloride and potassium picrate, (4) potassium chloride and potassium salt of iodeosin, (5) hydrochloric acid and mixtures of hydrochloric and picric acids, and (6) potassium chloride and potassium picrate to which varying amounts of potassium chloride had been added, have been investigated.

In the previous work, platinised platinum electrodes had been used for applying the external voltage. The maintenance of a constant current through the cell presented difficulties with these gassing electrodes because of capricious fluctuations of the internal resistance due to irregular gas bubbling at and near the electrodes. The use of platinum electrodes with salt solutions, *e.g.*, sodium chloride and sodium picrate presented further difficulties in that, on the passage of the current, acids and alkalis were formed at the anodes and cathodes respectively. The consequent introduction of the faster moving H° and OH' ions seriously affected the resistances of the original salt solutions and the potential gradient in the upper liquid showed considerable variations (*vide* Table II). The use of non-gassing reversible electrodes, *e.g.*, silver—silver chloride electrodes have eliminated these difficulties.

Measurements have been made with two moving boundary cells—one having a tube diameter of 18 mm., that of the other (the one constructed from a standard micro-burette) being only 6 mm. The effective distance of the first tube was measured as previously described (Mukherjee, *Proc. Roy. Soc.*, 1923, **A103**, 102) that of the narrow tube was obtained in a slightly different manner; the tube being filled with a solution whose specific conductivity had been previously determined, a current was passed and the potential difference between any two side-limbs, the effective distance between which was required, determined. Knowing the specific conductivity (k) of the solution and the area of cross-section (A) of the tube, the effective distance (l) was calculated from the equation,

$$P.D. = \frac{c\,l}{k\,A}.$$

RESULTS AND DISCUSSION.

(*a*) *The $V - x$ and $x - t$ Curves.*—The differential equations deduced in a previous section show that the assumptions underlying the theory being valid (*i*) the potential difference between two fixed planes, one in the 'leading' and the other in the 'indicator' solution, should vary linearly with the distance swept by the boundary; (*ii*) also the linear displacement of the boundary should vary proportionately with time. Experiment shows that the validity of these conclusions depends on the experimental conditions (*vide infra* ; also *cf.* Part I, this series).

(*b*) *Reproductibility of Results.*—The difficulties of reproducible measurements have been discussed in the previous paper (Mukherjee and co-workers, *loc. cit.*). Even with sharp and horizontal boundaries, where disturbances arising from diffusion and undue heating effects were presumably absent, the variations were often as high as 5 % of average values of the absolute rates of migration. Neglecting extreme variations, the observed deviations from average values seldom exceed 2 % in this work. The order of reproducibility is even more satisfactory when the initial indicator concentration is exactly what is required for complete adjustment (*vide infra*).

In calculating the transference numbers in the manner indicated the limitations of the procedure adopted have to be considered. With the more dilute solutions, the total current being comparatively small (of the order of 1 to 2 milliamperes), an error of 5—10 % is involved in measuring the current as the milliammeter used for this purpose reads directly to 1 milliampere only. The magnitude of the current (i') passing through the moving boundary cell has been calculated indirectly from the measured potential gradient (x) in the upper liquid from the equation $i'=XAk$; where A and k are respectively the area of cross-section of the tube, and the measured specific conductivity of the upper liquid which does not change. Table II shows satisfactory agreement between the observed (i) and calculated values (i') when the magnitude of the current is comparatively large ; with smaller currents deviations are observed. It will be seen that the transference numbers (Tcl$'$) obtained from the calculated values of the current are satisfactorily concordant. Incidentally, the above agreement between the observed and calculated values of the current illustrates the accuracy of the relevant measurements.

(*c*) *Effect of the Potential Gradient in the Leading Solution.*—In the previous paper (Mukherjee and co-workers, *loc. cit.*) it was suggested that the rates of migration probably depend on the potential gradient in the leading solution though Kohlrausch's theory contemplates no effect of the current provided that restoring effect is strong enough to give a satisfactory boundary. In this work this effect of the current has been studied in more detail. Table I gives the results of experiments with boundaries between 0·01 *N*-hydrochloric acid and 0·005 *N*-picric acid using different currents and hence different potential gradients in the leading solution.

TABLE I.

Boundary between 0·01*N*-HCl *and* 0·005*N*-HP.

Current in m. amp.	Pot. gr. in HCl (in volts).	$Vel' \times 10^5$ cm-sec.-volt-cm.	Max. % variation from average Vel'.	Current in m. amp.	Pot. gr. in HCl (in volts).	$Vel' \times 10^5$ cm-sec.-volt-cm.	Max. % variation from average Vel'.
8·5	0·89	81·2		14	1·43	80·7	
						81·1	
,,	0·88	81·2		,,	1·50	79·4 79·3	
,,	0·89	80·2 80·6 78·0*		,,	1·46	83·7* 78·4*	
					Average	80·1	+·8 –·9
,,	0·88	80·5 82·1*					
	Average	80·8	–0·8 +0·5	16	1·64 1·68	79·7 81·0	
10	1·05	80·8		,,	1·67	82·7	
,,	1·01	80·5 80·0			Average	8·08	
	Average	80·4	–0·5 +0·5				

It will be seen that the variations amongst average rates of migration under different potential gradients are of the order of the variations between results of independent measurements with the same potential gradient and are consequently within the limits of experimental error. Below the minimum current employed (8·5 ma) a sharp boundary could not be obtained owing to the restoring effect at the boundary being too weak to overcome the effects of diffusion and thermal convection, while with a current higher than sixteen milliamperes the boundary became convex upwards giving evidence of undue heating effects. The above observations that the results are independent of the applied potential gradient are in agreement with those of MacInnes and Smith (*loc. cit.*) according to whom the potential gradient has no effect when the solutions are initially adjusted. The hydrochloric and picric acid solutions in the above experiments were approximately of adjusted concentrations.

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* Rejected in calculating average values.

The wider tube was used.

TABLE II.

Boundary between NaCl *and* NaP.
(Wider tube used).

Combination.	Current in milliamps.	Pot. gr. in NaP.	$V_p' \times 10^5$ cm-sec-volt-cm.	$N_{cl}' \times 10^5$ cm-sec-volt-cm.	Maximum percentage variation from average V_{cl}'.
(1)** 0·02*N*-NaCl	8·0	3·11	80·25	37·2	
0·01*N*-NaP		3·03	80·2	39·1	
(2) ,,	8·05	3·52	81·5	33·7	
		3·39	81·7	35·0	
(3) ,,	8·05	3·48	81·3	33·9	
		3·24	81·3	36·4	
		3·48	83·0	34·7	
(4) ,,	7·05	3·29	82·4	31·8	
		3·22	82·9	32·7	
		3·13	83·8*	34·0	
(5) ,,	5·53	2·29	82·4	35·8	
		2·36	82·8	34·9	
		2·25		37·3	
		Average	82·1		−0·9
					+1·1
(6) 0·01*N*-NaCl 0·005*N*-NaP	3·6	2·76	85·1	38·6	
		2·84	84·9	37·4	
		2·94	84·7	36·1	
		Average	84·9		−·25
					+·25

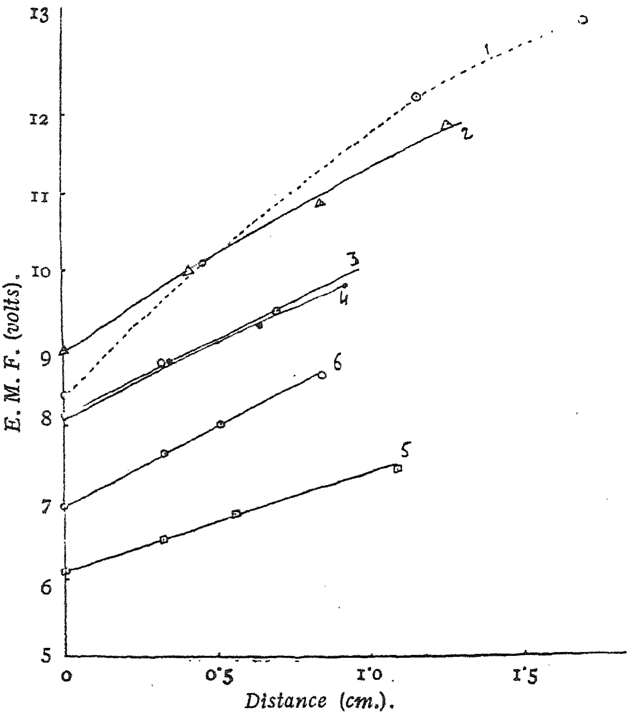
* Rejected in calculating average values.

** The curves have been correspondingly numbered in Fig. 1.

N. B. Expt. (1) was carried out using platinum electrodes; Ag-AgCl electrodes were used in the rest of the experiments.

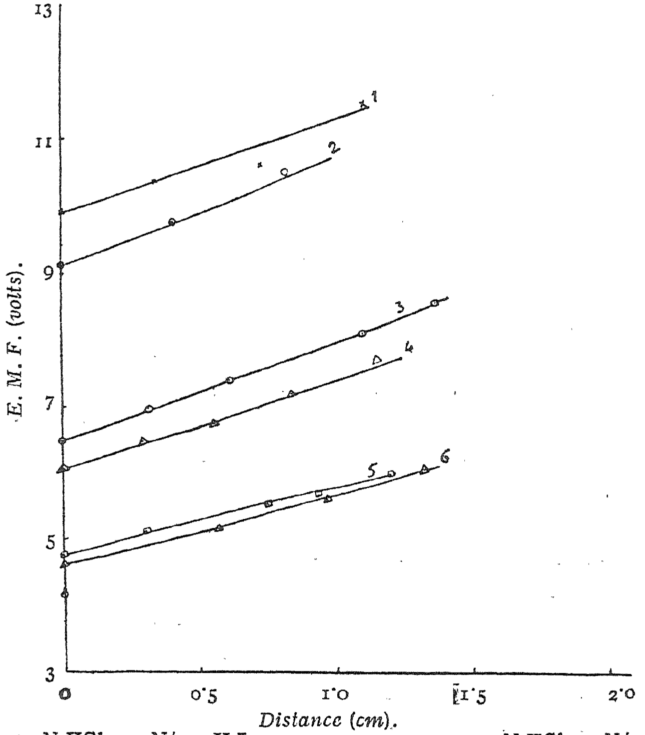
The need of using reversible electrodes for applying the external voltage for measurements with salt solutions has already been emphasised. Table II gives the results of experiments with sodium chloride and sodium picrate solutions using respectively platinum electrodes and silver—silver chloride electrodes. It will be seen that using the non-reversible electrodes (1) the potential gradients both in the sodium chloride and sodium picrate solutions diminish with time. Using reversible electrodes the potential gradient in sodium chloride remains remarkably constant (the values are not given in the table) ; the potential gradients in the sodium picrate solutions do not show any regular tendency to diminish. Satisfactory agreement is also to be found amongst the comparatively large number of values of the rate of migration of the chloride ion. Further—while the slopes of the V, x curves using the non-reversible electrodes (*cf.* curve 1, Fig. 1) tend to decrease, the corresponding curves with reversible electrodes are almost straight lines.

FIG. 1.



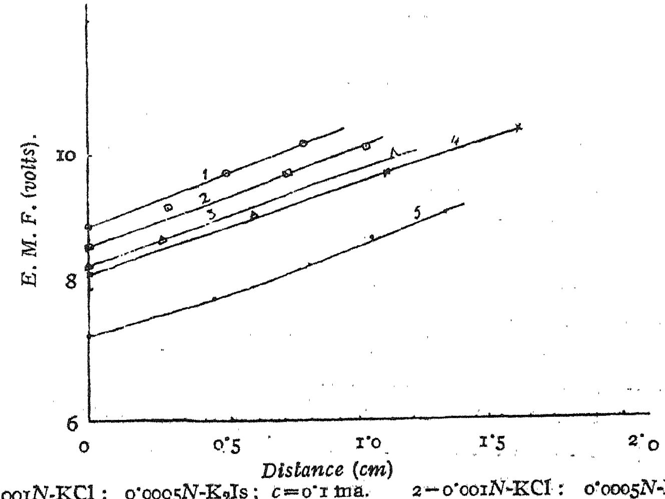
1 – *c*=8·0 ma. 2—0·02*N*-NaCl : 0·01 NaP ; *c*=8·05 ma
3—0·02 NaCl : 0·01 Na P ; *c*=8·05 ma. 4—*c*=7·05 ma.
5—0·02 Nacl : 0·01 Na P; *c*=5·53 ma.
6—0·01 NaCl : 0·005 NaP; *c*=3·6 ma,

FIG. 2.



1 and 2—0·01*N*-KCl : *N*/173-K_2Is ; *c*=1·15 ma. 3—0·01*N*-KCl : *N*/198-K_2Is ; *c*=0·725 ma. 4—0·01*N*-KCl : *N*/198-K_2Is ; *c*=0·71 ma. 5—0·01*N*-KCl : *N*/208-K_2Is ; *c*=0·575 ma. 6—0·01*N*-KCl : *N*/208-K_2Is.

FIG. 3.



1—0·001*N*-KCl : 0·0005*N*-K_2Is ; *c*=0·1 ma. 2—0·001*N*-KCl : 0·0005*N*-K_2Is ; *c*=0·1 ma. 3—0·005*N*-KCl : 0·0025*N*-K_2Is ; *c*=0·47 ma. 4—0·002*N*-KCl : 0·001 *N*-K_2Is ; *c*=0·2 ma. 5—0·002*N*-KCl : 0·001 *N*-K_2Is ; *c*=0·2 ma.

Effect of Tube Area.

The effect of the area of cross-section of the tube on the results has been studied in detail by Cady and Longsworth (*loc. cit.*). The numerous experiments of MacInnes and co-workers show that the tube area is an important factor in regulating the range of adjustment of an indicator solution for a leading solution of given concentration. The absolute rates of migration of the chloride ion given in the previous paper (Mukherjee and co-workers, *loc. cit.*) were distinctly lower than the accepted values at corresponding hydrochloric acid concentrations. It was thought that the discrepancy might arise from an injudicious selection of the tube area. With a tube of 11 mm. internal diameter Smith and MacInnes (*J. Amer. Chem. Soc.*, 1924, **46**, 1398) experienced serious difficulties arising from 'larger heating effects.' For measurements with acid solutions tubes of very small internal diameters (2 mm.) have been recommended. In view of these observations it was considered desirable to repeat the previous measurements with a much narrower tube (6 mm. bore). Referring to Tables I and IV which record the results of experiments with the wide and narrow tubes respectively, it will be found that using the same moving boundary system (0·01*N*-HCl and 0·005*N*-HP) the values of $V_{Cl'}$ with the narrower tube are considerably larger than with the wider tube and are nearer the accepted values.

Boundaries between Acid Solutions and Salt Solutions.

Comparison of absolute rates of migration of an anion (*e.g.*, the chloride ion) from measurements of 'acid boundaries' (*e.g.* between HCl and HP) and boundaries between salt solutions (*e.g.* between NaCl and NaP) is interesting in view of Mukherjee's idea of electrical separation at a sharp boundary. According to Mukherjee (*J. Indian Chem. Soc.*, 1928, **5**, 593) the electrical separation which arises from a difference of the transport number of the common ion in the two solutions forming the boundary should be comparatively small at an acid boundary since the mobility of the common hydrogen ion is so great compared with that of either of the unlike ions that its transport number is virtually the same in the two electrolytes.

Referring to Tables III and IV it will be found that using the same measuring tube the values for $V_{Cl'}$ are larger with the NaCl − NaP boundary than with the HCl − HP boundary. This result apparently contradicts a previous observation by Mukherjee (Mukherjee, *loc. cit.*)

that the discrepancy between the accepted value of the absolute rate of migration of an ion and that obtained by the boundary method arising from a separation of electricity at the boundary should be less for a boundary between acid than between salt solutions. The contradiction probably arises from an unequal initial adjustment of the indicator solution for a leading solution of the same chloride concentration. Thus comparing the system 0·01*N*-HCl: 0·005N-HP and 0·01*N*-NaCl: 0·005*N*-NaP, it is evident that the ratio [Cl′] / [P′] is different for the two systems in view of the comparatively small percentage dissociation of picric acid though the ratio [total chlorine] / [total picrate] is the same for both.

TABLE III.

Boundary between sodium chloride and sodium picrate.
(Narrow tube).

Combination	Current in milliamps.	*T*Cl′	Max. % variation from average *T*Cl′.	*V*Cl′ × 10⁵ cm/sec/volt/cm.	Max. % variation from average *V*Cl′.	*V*p′ × 10⁵ cm/sec.
0·05 *N*-NaCl 0·025 *N*-NaP	4·05	0·597		81·3 81·6		
,,	4·05	0·593		79·9 78·5*		
,,	4·05	0·587		79·4		37·1
,,	3·95	0·591		80·4 80·0		29·8 31·3
,,	3·95	0·589		80·1 79·6		29·2 29·9
	Average	0·59·1	−0·7 +0·8	Average 80·3	−1·1 +1·6	
0·02*N*-NaCl 0·01*N*-NaP	1·7	0·600		84·2 85·5		31·5
,,	1·1	0·605		84·3		30·9 32·4
,,	1·2	0·610		85·7		32·2
	Average	0·605	−0·8 +0·8	Average 85·0	−0·9 +0·8	33·0
0·01 *N*-NaCl 0·005 *N*-NaP	0·95	0·593		88·3		33·2
,,	0·95	0·600		86·7 86·8		34·9 36·6
	Average	0·597	−0·8 +0·7	Average 87·2	−0·45 +1·2	

* Rejected in calculating the average values.

TABLE IV.

Boundary between hydrochloric acid and picric acid.
(Narrow tube).

Combination.	Current in milliamps.	$T_{Cl'}$.	$V_{Cl'} \times 10^5$ cm/sec volt/cm.	$V_{p'} \times 10^5$ cm/sec/volt/cm.
0·02*N*-HCl 0·01*N*-HP	5·5	0·172	81·6	38·5
			80·7	38·0
,,	5·5	0·171	81·2	35·3
			79·7	35·3
		Average 0·1715	Average 80·8	
0·01*N*-HCl 0·005*N*-HP	2·55	0·171	85·6	35·5
			85·6	
			83·9	
			Average 85·0	

TABLE V.

Boundary between potassium chloride and potassium picrate.
(Narrow tube).

Combination.	Current in milliamps.	$T_{Cl'}$.	$V_{Cl'} \times 10^5$ cm/sec/volt/cm.	$V_{p'} \times 10.$ cm/sec/volt/cm.
0·05*N*-KCl 0·025*N*-KP	4·5	0·501	80·3	32·3
				32·3
,,	4·5	0·504	80·4	30·6
				31·2
				31·0
		Average 0·503	Average 80·35	
0·02*N*-KCl 0·01*N*-KP	1·9	0·512	85·2	38·9
			83·2*	38·3
,,		0·496	86·2	36·6
			85·1	
		Average 0·504	Average 85·5	

Referring to Tables I and II (results with the wider tube) and also Tables III and IV (results with the narrower tube) it will be found that the values for $V_{Cl'}$ from a particular measurement generally diminish chronologically with the moving boundary system HCl − HP, whereas the effect is less pronounced with the NaCl − NaP system. Also with the HCl − HP system the successive values of the potential gradient in the picric acid layer show a tendency to decrease (*cf.* Part I, this series). Since the potential gradient in the picric acid layer is obtained from equation (*iv*), a gradual diminution of this potential gradient connotes a diminution in $\delta v/\delta x$, the potential gradient in HCl remaining constant. The cause of the diminution in $\delta v/\delta x$ (*i.e.*, the change in P. D. between side-limbs 2 and 3 for a centimetre displacement of the boundary) should be sought in the boundary itself. A mixed layer whose specific resistance σM is less than the original specific resistance σ_2 and whose thickness gradually increases, is perhaps responsible for the progressive diminution in $\delta v/\delta x$. The comparatively stronger heating effects at an acid boundary than at a boundary between salt solutions favours the formation of the mixed layer in the former case.

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* Rejected in calculating average values.

Automatic Concentration Adjustments at the Boundary.

TABLE VI

Boundary between 0·01 *N-hydrochloric acid and picric acid* (Wide tube).

Conc. of HP.	Pot. gr. in HP.	$T_{Cl'}$.	$V_{Cl'} \times 10^5$ cm./sec./volt/cm.	$V_{P'} \times 10^5$ cm./sec./volt/cm.
$N/200$	1·79		80·8 (Table) I	
$N/220$	1·94	0·184	87·6	34·2
	1·88		86·6	34·9
	1·81		85·5	35·7
,,	1·74	0·181	87·0	37·1
	1·86		86·9	34·9
	1·75		86·1	35·7
			Average 86·6	
$N/235$	1·99	0·188	90·8*	34·9
	1·85		87·6	34·4
	1·81		87·1	34·9
	1·74		84·5	35·2
,,	1·83	0·180	88·1	34·4
	1·73		87·3	36·1
$N/250$	1·67	0·191	96·7	29·2
	1·56		95·9	30·9
	1·50		92·3	30·9
,,	1·73	0·189	93·7	27·8
	1·50		93·6	31·9
	1·52		92·9	31·3

* Rejected in calculating average values.

According to the theory of the method as developed by Kohlrausch (*loc. cit.*), the movement of the boundary should be independent of the nature and concentration of the ‘indicator’ solution, *i.e.*, for a given concentration of the leading solution there should be no limit to the range of concentration adjustment of the indicator solution. The work of previous investigators shows, however, that the range is limited depending upon the relative strengths of the restoring effect and the disturbing influences, *e.g.*, diffusion, convection etc., operating at the boundary. The results of moving boundary experiments have been often found to be misleading due to a failure to secure the necessary condition of adjustment. The low values of $V_{Cl'}$ given in the previous paper (Mukherjee and co-workers, *loc. cit.*) might be referred to this cause. It was, therefore, considered desirable to repeat the previous measurements with varying concentrations of the indicator solution with a leading solution of a given concentration.

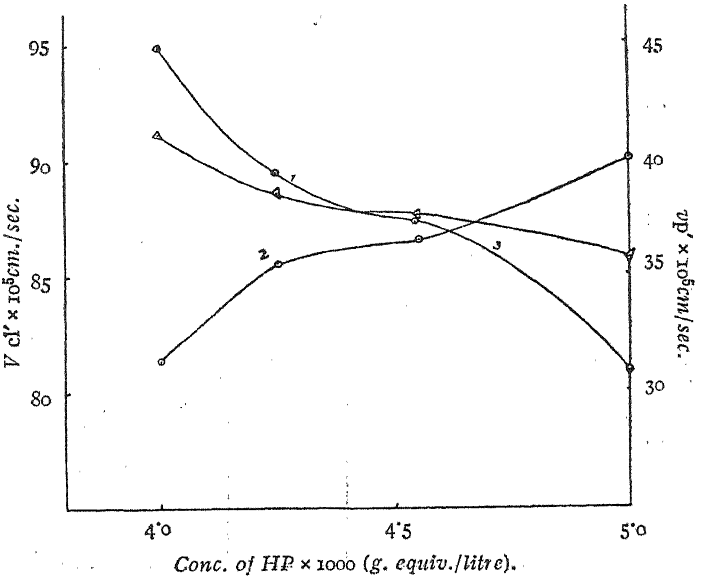
Table VII.

Boundary between 0·01*N-hydrochloric acid and picric acid.*
(Narrow tube).

Conc. of HP	Pot.gr. in HP	$T_{Cl'}$.	$V_{Cl'} \times 10^5$ cm./sec./volt/cm.	$V_{P'} \times 10^5$ cm./sec./volt/cm.
N/100-HCl, *N*/200-HP	3·84	0·171	85·6 85·6 83·9	35·5
” ”	3·80 3·60	0·176	85·5 82·0	37·4 40·4
N/100-HCl, *N*/220-HP	3·84	0·181	87·7 86·8	38·1
” ”	3·69	0·181	87·3 87·5 Average 87·3	39·7
N/100-HCl, *N*/250-HP	3·47	0·186	90·2 98·5	43·1
” ”	3·65	0·186	91·8 90·5	42·1
N/100-HCl, *N*/277-HP	3·99	0·183	88·8	37·8

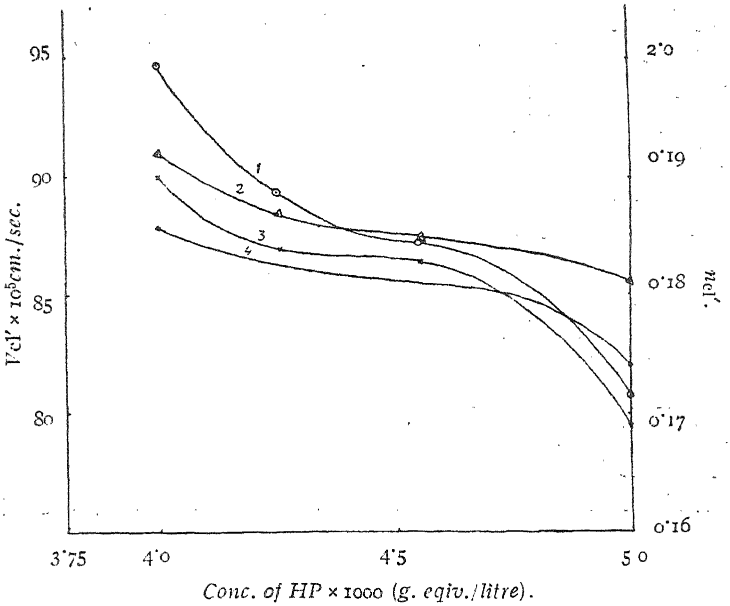
Referring to Tables VI and VII it will be seen that the values for $V_{Cl'}$ very largely depend on the initial picric acid concentration. The correct value is obtained within a very limited range of the indicator ion concentration, the range being smaller with the wider than with the narrower tube. The previously observed discrepancy (*cf*. Part I, this series) from the correct value does not arise, therefore, from any inherent defect of the method but is rather to be referred to a failure to secure the necessary condition of adjustment. The curves showing the range of adjustment are given in Figures 4 and 5. As already stated the range (the flat portion of the curve) is smaller with the wider than with the narrower tube. With picric acid concentrations, higher and lower than the adjusted concentration, the values for $V_{Cl'}$ are lower and higher than the correct value. With the wider tube outside the range of adjustment, it is interesting to find that the rates of migration of the picrate ion tend to diminish when the corresponding values for $V_{Cl'}$ tend to increase and *vice versa* (curves 1 and 2, Fig. 4).

FIG. 4.



Curves 1–3 refer to $V_{Cl'}$ (wide tube), $V_{p'}$ (wide tube) and $V_{Cl'}$ (narrow tube) respectively.

FIG. 5.



Curves 1—4 refer to Vcl' (wide tube), Vcl' (narrow tubs), ncl' (wide tube) and ncl' (narrow tube) respectively.

FIG. 6.

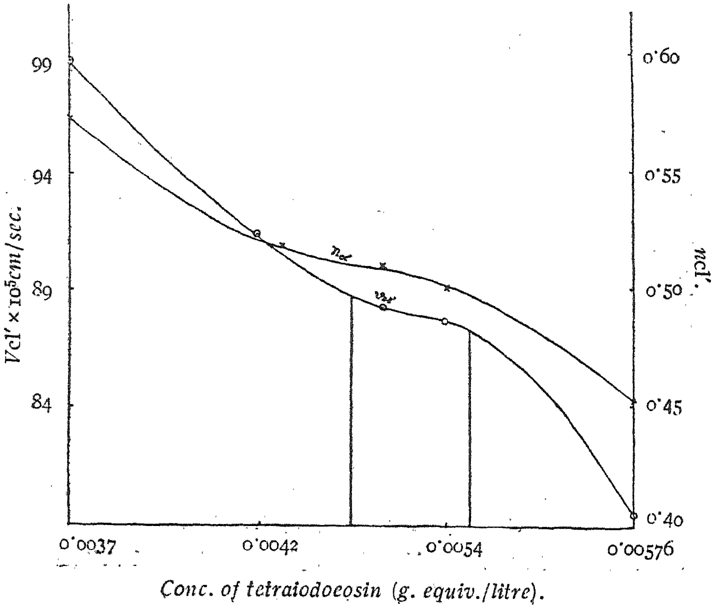


TABLE VIII.

Boundary between 0·01N—potassium chloride and K—tetraiodeosin (potassium salt).

Conc. of KIs.	Current in* milliamps.	Pot gr. in KIs in volts.	T_{cl}'.	$V_{cl}' \times 10^5$ cm./sec./volt/cm.	$V_{Is}' \times 10^5$ cm/sec.°volt/cm.
† (1) *N*/173	1·15	3·45	0·453	79·8	49·0
		3·33		75·7	48·2
		3·59		75·0	44·3
(2) „	1·15	3·61	0·453	79·0	44·9
		3·77		75·5	40·7
(3) *N*/198	0·725	2·76	0·501	87·3	40·7
		2·76		87·5	40·8
		2·75		87·7	41·1
		2·79		87·9	40·6
(4) „	0·71	2·49	0·499	88·1	43·6
		2·41		87·5	44·8
		2·53		88·4	43·1
		2·63		87·8	41·2
				Average 87·8	Average 42·0
(5) *N*/208	0·575	2·13	0·508	88·1	42·7
		2·00		86·9	44·9
		1·96		86·6	45·7
		1·99		85·5	44·4
(6) *N*/230	0·675	3·0	0·516	90·4	42·9
		2·51		89·8	
		2·59		87·4	
(7) „	0·71	2·94	0·524	92·5	42·4
		2·71		92·0	

With 0·01*N*-KCl as the leading solution and tetraiodeosin solutions of varying concentrations as the indicator electrolyte, the range of adjustment (Table VIII and Fig. 6) is appreciably larger and within this range the values for V_{cl}' agree with those obtained from the moving boundary systems NaCl−NaP and KCl−KP and also with the correct value within the limits of experimental error. It is interesting to note that within the range of adjustment the results are very satisfactorily regular and reproducible. Referring, for instance, to Table VIII it will be observed that within this range (*i*) mutually agreeing values for V_{cl}'

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* Calculated as indicated.

† The $v-x$ curves have been correspondingly numbered in Fig. 2.

N.B. Narrow tube used in these measurements.

are obtained which also agree with the correct value ; outside this range the agreement is far from satisfactory and the values diminish chronologically ; (*ii*) the successive potential gradients in the indicator solution do not show any regular tendency to diminish, whereas outside the range of adjustment the values decrease chronologically (*vide* Figs. 2 and 3); (*iii*) even the values for the rates of migration of the 'indicator ion' which generally show capricious variations are fairly concordant within the range of adjustment. In the light of these observations the condition of adjustment appears to assume a peculiar significance.

To investigate further the effects of automatic concentration adjustments, a boundary between 0·01*N*-sodium chloride and 0·005*N*-sodium picrate solutions was initially formed just below the side-limb 2 and the potential gradient in the upper liquid determined with the boundary

TABLE IX

Boundary between potassium chloride and K—*tetraiodeosin.*

Combination.	Current in milliamps.	Pot. gr. in KIs in volts.	*V*cl′ × 10³ cm/sec/volt/cm	Max. % variation from average *V*cl′.	*V*Is × 10⁵ cm/sec/volt/cm.
0·005*N*-KCl 0·0025*N*-KIs	0·47	2·76	89·5		46·1
			88·6		
,,	0·47	2·84	89·7		45·0
		2·67	90·4		48·3
		2·94	90·3		43·8
		Average	89·1	−0·6 +1·4	
0·002*N*-KCl 0·001*N*-KIs	0·20	2·80	91·4		47·6
		2·95	91·0		45·1
		2·91			45·0
,,	0·20	2·92	91·4		46·8
		2·89	90·9		47·0
		Average	91·2	−0·3 +0·2	
0·001*N*-KCl 0·0005*N*-KIs	0·10	3·34	93·1		43·8
		3·11	92·6		46·3
		3·07			
,,	0·10	3·20	92·5		46·1
		3·22	91·8		45·5
		Average	92·5	−0·78 +0·6	

Narrow tube was used

in this position. The changes in P. D. between side-limbs (1) and (2), and side limbs (1) and (3) due to given linear displacements of the boundary ($\delta v/\delta x$) were recorded. On adding these two sets of values of $\delta v/\delta x$ to the previously determined potential gradient in the upper liquid, two sets of values of the potential gradient in the sodium picrate solution were obtained which being combined with the observed displacements of the boundary gave two sets of values for the rate of migration.

TABLE X.

Time in secs.	Pot. gr. in NaP from changes in P. D. between 1 & 2.	Pot. gr. in NaP from changes in P. D. between 2 & 3.	$Vp' \times 10^5$ cm/sec. from $\delta v/\delta x$ from 1 & 2.	$Vp' \times 10^5$ cm/sec. from $\delta v/\delta x$ from (1) & (3).
259	1·97	1·40	34·2	41·4
544	1·87	1·43	35·1	40·8
795	1·75	1·39	36·9	41·9
1135	1·65	1·37	37·5	41·5

It will be observed that the average potential gradient in the sodium picrate solution is greater in a comparatively thin layer of this solution near the boundary (the $\delta v/\delta x$ values being obtained from potentiometric measurements between side-limbs 1 and 2) than the gradient in a comparatively longer column between the boundary and the lowest side-limb (from potentiometric measurements between side limbs 1 and 3). This indicates that the concentration adjustments (in this case a dilution of the picric acid solution) take place in a layer of the solution behind the boundary and contiguous to it. The picrate ion mobilities calculated from a linear displacement of the picrate ions under larger potential gradients at and near the boundary should be smaller (*vide* Table X) than those calculated with the aid of smaller average gradients in a comparatively long column of the pictrate solution.

The effect of concentration adjustments at and near the boundary is brought out more clearly by the results given in Table XI.

TABLE XI

Combination.	Current observed (i).	Sp. cond. of upper liquid in mhos (K_1).	Pot. gr. in upper liquid in volts (X).	Current calculated ($i' = XAK_1$).	Tcl' from i'.	Pot. gr. in the lower liquid (X').	Obs. sp. condty. of the lower liquid in mhos (K_2).	Calc. sp. condty. of the lower liquid ($K_2' = i'/AX'$).
0·05N-KCl 0·025N-KP	4·5	0·0077	1·74	4·49	0·502	4·4 4·32	0·0028	0·0031
,,	4·5	0·0077	1·75	4·51	0·503	4·61 4 51 4·49	0·0028	0·0029
0·02N-KCl 0·01N-KP	1·88	0·0033	1·73	1·89	0·502	3·79 3·76	0·0077	0·0014
,,	1·88	0·0033	1·73	1·89	0·492	4·33 4·26	0·0077	0·0013
,,	1·95	0·0033	1·74	1·90	0·508	4·11	0·0077	0·0013
0·01N-KCl 0·005N-KP	0·85	0·0017	1·50	0·84	0·502	3·8 3·73 3·75	0·00059	0·00066
,,	0·85	0·0017	1·50	0·84	0·504	3·45	0·00059	0.00073
0·01N-KCl 0·005N-KIs	0·73	0·0017	1·28	0·72	0.501	2·76 2·76 2·75 2·79	0·00058	0·00079
,,	0·70	0·0017	1·23	0·69	0·502	2·49 2·41 2·53 2·63	0·00058	0·00084
0·005N-KCl 0·0025N-KIs	0·43	0·00086	1·48	0·42	0·501	2·76	0·00030	0·00046
,,	0·41	0·00086	1·42	0·40	0·502	2·84 2·67 2·94	0·00030	0·00043
0·002N-KCl 0·001-KIs	0·20	0·00035	1·49	0·18	0·502	2·8 2·95 2·91	0·00012	0·00018
,,	0·20	0·00035	1·49	0·18	0·502	2·92 2·89	0·00012	0·00018
0·001N-KCl 0·0005N-KIs	0·10	0·00018	1·50	0·093	0·507	3·34 3·07	0·000061	0·000083
,,	0·10	0·00018	1·59	0·094	0·504	0·2 3·22	0·000061	0·000088

In the eighth column of the above table are given the measured initial specific conductances (K_2) of the indicator solutions. Changes in these specific conductances on a current being passed would indicate concentration adjustments. Knowing the potential gradient X' in the indicator solution in the usual manner, the area of cross-section (A) of the tube and the current i, the new specific conductivity K'_2 can be calculated with the aid of the equation $K'_2 = i/AX'$. This method of determining the changed specific conductivity does away with the need of actual conductivity measurements between small electrodes sealed into the measuring tube (*cf.* Cady and Longsworth, *J. Amer. Chem. Soc.*, 1929, **51**, 1656; Hartley and co-workers, *Trans. Faraday Soc.*, 1934, **30**, 648), a procedure which is not altogether free from objections.

Agreement of Observed Values of $V_{Cl'}$ *with Accepted Values.*

Onsager's equation for uni-univalent electrolytes takes the form

$$\lambda = \lambda_0 - (0{\cdot}164\ \lambda_0 + 26{\cdot}81)\ \sqrt{2c} \text{ at } 35^\circ,$$

evaluating for D, T, λ etc.; where λ and λ_0 are the mobilities at the concentration c and at infinite dilution respectively. If the mobility or the absolute rate of migration of an ion be plotted against $\sqrt{c}$, a straight line should result whose intercept on the axis of rate of migration should give the rate of migration at infinite dilution. In the following table the observed absolute rates of migration of the chloride ion obtained under conditions of adjustment have been summarised.

TABLE XII.

Conc. in g. equiv./litre. (c).	$V_{Cl'} \times 10^5$ cm./sec./volt./cm.		$\sqrt{c}$.
0·05	80·3	(Tables III—V)	0·224
0·02	85·0	(Tables III—V)	0·142
0·01	87·7	(Table VIII)	0·10
0·005	89·1	(Table IX)	0·071
0·002	91·2	(Table IX)	0·045
0·001	92·5	(Table IX)	0·031

The curve (*vide* Fig. 7) obtained by plotting the above values of $V_{Cl'}$ against corresponding values of $\sqrt{c}$ when extrapolated yields a value for $V_{Cl'}$ $93{\cdot}76 \times 10^{-5}$ cm./sec. which agrees fairly well with the correct value.

FIG. 7.

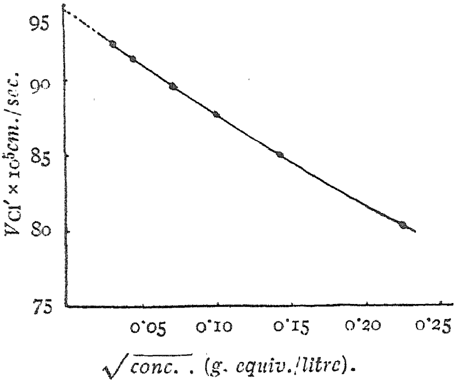


TABLE XIII.

Boundary between 0·01-*N* HCl *and mixture of* HCl *and picric acid.* (Narrow tube).

Current in milliamps.	Pot. gr. in HCl.	Pot. gr. in the mixture.	$V_1 \times 10^5$ cm/sec/volt/cm.	$V_2 \times 10^5$ cm/sec/volt/cm.
6	0·65	0·82	41·8	33·0
14	1·55	1·96	44·77	35·4
		2·00	45·7	35·4
		2·00	43·1	33·3
9	0·99	1·14	41·1	35·5
7·5	0·94		42·6	
			38·3	
11	1·20	1·46	42·7	35·0
		1·47	41·1	33·7
		1·48	43·6	35·5

TABLE XIV.

Boundary between 0·01-*N* HCl *and equiconducting mixture of* HCl *and picric acid.* (Narrow tube).

11·5	1·24	2·0	49·3	30·6
		1·98	50·1	31·6
11·5	1·25	2·04	49·1	30·1
		1·90	50·4	33·2
6·35	0·70	1·14	49·4	30·6
		1·21	40·2	

Moving Boundary Experiments with Mixtures of Electrolytes.

Moving boundary experiments with mixtures of electrolytes are of interest as the results of such experiments are likely to throw light on the conditions obtained at and near the boundary in measuring the cataphoratic speeds of colloidal particles by the boundary method. A colloidal solution contains electrical carriers of several categories and it thus simulates a mixture of electrolytes.

Moving boundary experiments with mixtures of electrolytes have been carried out by MacInnes, Cowperthwaite and Shedlovsky (*J. Amer. Chem. Soc.*, 1929, **51**, 2671) in determining the transference number of the chloride ion in mixtures of sodium and potassium chlorides. Transference number of the hydrogen ion in mixtures of hydrogen and pottassium chlorides have been determined by MacInnes and Longsworth (*Chem. Rev.*, 1932, **11**, 171).

Table XIII gives the results of experiments with boundaries between a 0·001*N*-hydrochloric acid solution and a mixture of hydrochloric and picric acids having the composition : 100 c.c. of the mixture obtained by mixing 90 c.c. of 0·01*N*-HCl and 10 c.c. of 0·05*N*-picric acid such that the concentration of picric acid in the mixture was approximately the adjusted concentration for 0·01*N*-hydrochloric acid. The boundary in the case of the mixture was not as sharp as with the pure electrolytes owing to the restoring effect being much weaker; a broad band was generally observed. It will be found from Table XIII that on combining the observed speed of the boundary with (*i*) the potential gradient in the upper liquid and (*ii*) with that in the mixture, two sets of values are obtained none of which show any agreement with accepted values for the rate of migration of the chloride ion, though an approximate agreement is to be observed with the picrate ion mobility. Table XIV records the results of investigations with a boundary between 0·01*N* hydrochloric acid and an initially equiconducting mixture of hydrochloric and picric acids containing approximately 0·005*N*-picric acid. The values in this case also show closer agreement with the picrate ion mobility than with that of the chloride ion. Finally the effect of addition of varying amounts of the leading solution to the indicator electrolytes has been studied. Table XV shows that in the case of a boundary between 0·02*N*-KCl and 0·01*N*-potassium picrate solutions the addition of increasing quantities of the potassium chloride is marked by a progressive diminution in the values for V_{Cl}. Table XVI records similar observations with 0·01*N*-KCl and 0·005*N*-potassium picrate to which increasing quantities of the KCl have been added (*vide* Fig 9). Also the slopes of the corresponding *v*-*x* curves (Fig. 8) show a tendency to decrease though the curve (given in dotted lines) for the same combination without addition of KCl to the picrate solution is practically linear.

TABLE XV.

Boundary between 0·02*N potassium chloride and* 0·01*N-potassium picrate to which varying amounts of* KCl *have been added.*
(Narrow tube).

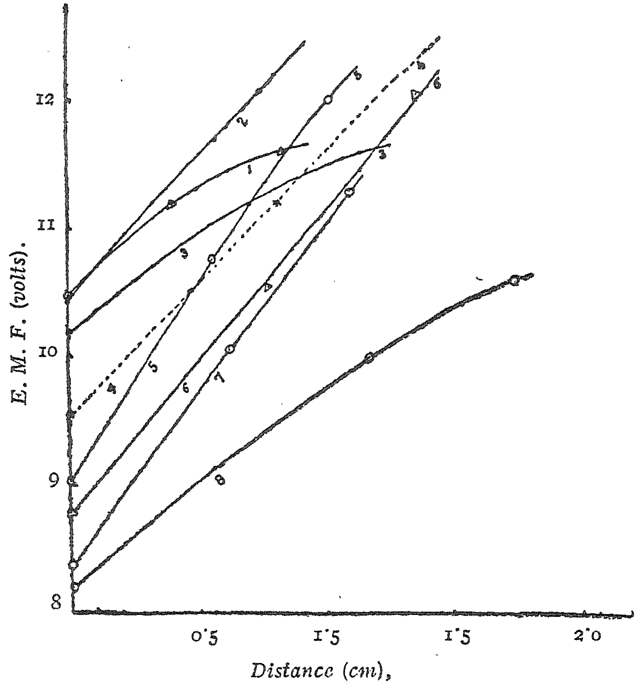
C_{KCl}/C_{KP} in the indicator solution.	Pot. gr. in KCl in volts.	Pot. gr. in the mixture in volts.	$Vcl' \times 10^5$ cm/sec/volt/cm.	$Vp' \times 10^5$ cm/sec/volt/cm.
2·5%	1·89	4·12 4·25	84·3 83·8	38·7 37·3
2·5	1·89	4·03 4·03	83·4 82·5	39·0 38·7
5	1·89	5·05 4·57	80·8 79·8	30·3 36·2
5	1·92	4·62 4·58	81·2 78·6 77·0	33·8 33·0
10	1·91	3·33 3·13	72·1 68·3	41·3 41·6
10	1·96	3·73 3·31	72·0 70·8	37·3 41·4
10	1·74	3·27 3·09	69·3 68·9	36·7 38·6

TABLE XVI.

Boundary between 0·01*N-potassium chloride and* 0·005*N-potassium picrate to which varying amounts of* KCl *have been added.*
(Narrow tube).

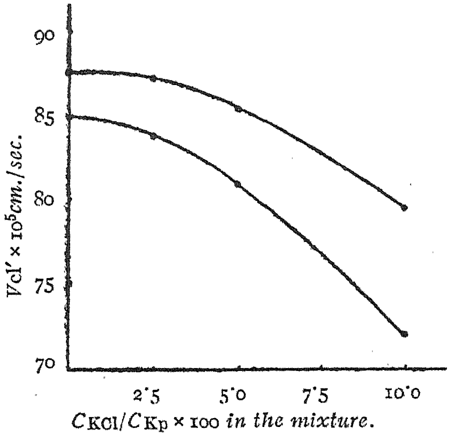
C_{KCl}/C_{KP} in the indicater solution.	Pot. gr. in KCl in volts.	Pot. gr. in the mixture in volts.	$Vcl' \times 10^5$ cm/sec/volt/cm.	$Vp' \times 10^5$ cm/sec/volt/cm.
2·5%	2·09	4·81	87·4 86·6	38·1
2·5	2·08	4·89	87·3 88·1 87·9	37·3
5	2·02	4·52	85·4 83·5	38·2
10	2·04	4·22 4·08	79·6 78·2	38·6 39·1
10	2·05	4·65 4·55	80·0 77·8 77·1	34·5 35·1

FIG. 8.



1—0·02N-KCl : 0·01N-KP (with 0·001N-KCl) ; c=2·3 ma.
2— „ „ : „ „ (with 0·00025N-KCl) ; c=2·15 ma.
2— „ „ : „ „ (wtth 0·001N-KCl) ; c=2·2 ma.
4— „ „ : „ KCl.
5— „ „ : 0·01N-KP (with 0·005N-KCl ; c=2·2 ma.
6— „ „ : „ „ (with 0·00025N-KCl) ; c=2·15 ma,
7— „ „ : „ „ (with 0·0005N-KCl) ; c=2·2 ma.
8— „ „ : „ „ (with 0·001N-KCl) ; c=2·2 ma.

FIG 9.



The upper and lower curves refer respectively to 0·01N-KCl : 0·005N-KP (containing KCl) and 0·02N-KCl ; 0·01N-KP (containing KCl).

In the light of the above results, the chronological diminution in the values for V_{Cl} in independent measurements frequently observed in this and the previous work (Mukherjee and co-wokrers, *loc. cit.*) is to be referred to a progressive ingress of the upper liquid into the indicator electrolyte. A detailed discussion of these aspects of the problem has to be deferred till further experiments, now in progress, have been completed.

SUMMARY.

1. Rising boundaries between pure solutions of (1) hydrochloric acid and picric acid, (2) potassium chloride and potassium picrate, (3) sodium chloride and sodium picrate, (4) potassium chloride and potassium compound of tetraiodeosin as also boundaries between suitably chosen mixtures of the above electrolytes have been investigated following Mukherjee's method of measuring the cataphoretic speeds of colloidal particles.

2. The variations of the potential difference between two fixed planes between which the boundary was located with the linear displacement of the boundary have been directly measured and the absolute rates of migration of the 'leading' and 'indicator' ions have been calculated from such variations and the observed rate of motion of the boundary. Simultaneous measurements of the transference numbers of the leading ion have been made from observations of the volume displacement of the boundary.

3. The effects of (*a*) the area of cross-section of the tube, (*b*) the strength of the current and (*c*) the addition of small quantities of the leading solution to an approximately adjusted solution of the indicator electrolyte, have been studied. Experiments throwing light on the mechanism of concentration adjustments at and near the boundary have been carried out. The need of securing the condition of adjustment for obtaining correct and reproducible results has been emphasised. It has been shown that the method gives accurate values of absolute rates of migration of ions and may be applied to ascertain the changes taking place in different layers of the solutions at the boundray. As in the MacInnes method here also the transference numbers can be simultaneously obtained.

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The preparation of Thorium Phosphate Gels.

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Thorium phosphate gels were first prepared by Satya Prakash (*J. Indian Chem. Soc.*, 1929, **6**, 587)by mixing solutions of suitable concentrations of thorium nitrate and potassium phosphate. He first obtained a precipitate which disappeared on shaking and resulted in the formation of a more or less opaque solution. On keeping the solution for sometime, it set to a firm transparent gel imbibing within itself all the liquid present in the solution.

It has been found that these gels can be easily prepared if a solution of phosphoric acid is used instead of that of potassium phosphate. In this case only a slight precipitate is obtained and it disappears quickly on shaking. The resulting solution instead of being opaque is quite clear and sets to a firm transparent gel which does not synerise.

It will be seen that in the above methods of preparation, the precipitate of thorium phosphate is peptised to a sol by the hydrogen and thorium ions present in the gel-forming mixture and this process is greatly accelerated by shaking. But it is known that thorium phosphate is insoluble in dilute mineral acids and dissolves readily in the concentrated ones. Therefore, it should be possible to prepare thorium phosphate sol by diluting a solution of thorium phosphate in concentrated acids. In this case the colloidal micelles will be formed by the aggregation or condensation of the molecules of thorium phosphate.

For this purpose, a saturated solution of pure thorium phosphate (7·2 g.) was made in hydrochloric acid (400 c.c. of 4 *N*-HCl) and 1 c.c. of this solution was diluted to different extent by the addition of distilled water. Nothing separated out when 1 c.c. of the solution was added to 1 c.c. of water. But when it was added to 2 c.c. of water slightly opalescent, hydrated flakes separated out. This observation definitely disproves the statement (Mellor, "Inorganic Chemistry", vol. VII, p. 252) that a solution of thorium phosphate in a strong mineral acid does not throw out the precipitate on dilution.

On further increasing the dilution by 1 c.c. upto 30 c.c., it was found that thorium phosphate gels were formed. Some of these gels were slightly opalescent, while those formed with higher dilution were quite transparent and rigid. When 1 c.c. of the solution was diluted with more than 30 c.c. of water, only a transparent and homogeneous viscous mass was obtained, *i.e.*, no visible separation of the precipitate took place.

From a long series of experiments on precipitations, Von Weimarn has derived the expression

$$N = V\frac{P}{L}$$

where N represents the "form coefficient" of the precipitate, V is a function of the viscosity of the reaction system, P, the excess of concentration of the substance to be precipitated and L its solubility. According to the above equation if N is large, a gel is formed which cannot be resolved by the microscope while if it is small, a precipitate, which may be amorphous or gelatinous, is obtained.

The value of N increases as V and P increase and L decreases. Since the solubility of thorium phosphate in dilute acids is less than that in concentrated ones, the value of L decreases and of P increases when a solution of thorium phosphate in concentrated acids is diluted. Further the value of V is large because thorium phosphate has a great tendency for hydration. Thus in the case of thorium phosphate, conditions are favourable for the formation of a gel by the dilution method. These observations, therefore, support Weimarn's theory in a qualitative manner. These experiments also show that the gelling substance is a soild and hence in the case of these gels the liquid-liquid theory of gel structure cannot be upheld.

An interesting observation on the above mode of preparing the gels was made when thorium phosphate gels prepared from thorium nitrate and phosphoric acid were dehydrated. Two sets of gels (*i*) containing the same amount of phosphoric acid and different amounts of thorium nitrate and, (*ii*) containing the same amount of thorium nitrate and different amounts of phosphoric acid, were desiccated over phosphorous pentoxide and they were observed to shrink and lose their form. When the volume of these gels was reduced to about one sixth of the original, the whole mass was converted to a clear transparent solution. The liquid phase did not appear in all gels simultaneously; it appeared earliest in gels containing the least amount of phosphoric acid and the largest amount of thorium nitrate.

The appearance of the liquid phase is due to the fact that as the water content of the gels decreases on dehydration, the H-ion concentration in the gel is increased and thorium phosphate first passes into a colloidal state and then goes into solution. On increasing the amount of phosphoric acid, a greater amount of thorium phosphate is formed and this requires a larger H-ion concentration for solution and hence the appearance of the liquid phase is delayed. Large amounts of thorium nitrate cause the appearance of this phase earlier as thorium ions assist the peptising action of H-ions. These observations conclusively show that thorium phosphate gels can only be obtained when the H-ion concentration of the gel-forming mixtures is below a definite value.

If water is slowly added to the solution, obtained by dehydrating a gel or if the solution is put in an atmosphere of water vapour at reduced pressure, it absorbs water, increases in volume and sets down to a firm gel once again. Thus the reversible sol-gel transformation which is peculiar to organic jellies and is caused by changes in temperature, can be observed in thorium phosphate gel, as well, by dehydrating and hydrating the gel prepared from thorium nitrate and phosphoric acid.

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Received November 13, 1935.

A Modified Micro-method for the Estimation of Nitrogen in Soil.

BY SRISH KUMAR SAHA.

In course of the analysis of a number of soil samples containing a low percentage of nitrogen, it appeared to us to be of interest to ascertain the applicability and also the accuracy of Micro-Kjeldahl methods for such estimation. A number of parallel experiments showed that the results of micro- and macro-estimations were absolutely concordant.

The samples were dried at 100°-110° and passed through a sieve of 100 mesh. In view of the low percentage of nitrogen, 0·1 to 0·2 g. of each sample was weighed out in an ordinary analytical balance. The rest of the procedure was exactly as in Pregel's Micro-Kieldahl. The final titrations were made with N/70 solutions with Wesslow's indicator (methylene blue-methyl red). The results are given below in a tabular form.

No. of sample.	Macro-estimation according to the method of A. O. A. C.		Micro-estimation	
	Wt. taken.	% N.	% N.	Wt. taken.
1	6·653 g.	0·1840	0·1837	0·1443
2	7·8717	0·1621	0·1620	0·1510
3	6·5230	0·1577	0·158	0·1356
4	5·5472	0·5082	0·508	0·0728
5			0·28	0·1645
6			0·182	0·2139
7			0·376	0·1704
8			0·243	0·1525
9			0·0442	0·2030
10			0·0367	0·1364

My thanks are due to Sir P. C. Ray for the kind interest he has taken in this work.

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Received December 2, 1935.

Analytical Uses of Nessler's Reagent. A Preliminary Note.

By M. Goswami and B. C. Das-Purkayastha.

It has been shown by one of us (M. Goswami) in a previous paper (*J. Indian Chem. Soc.*, 1935, **12**, 714) that potassium mercuric iodide solution could be very advantageously used to distinguish ketones from aldehydes which always give mercury and further that it could be utilised for quantitative estimation of glucose. The reaction has now been extended for the estimation of fructose and cane sugar and very concordant results have been obtained. The method will now be applied for the estimation of pentose and other disaccharides as also other important aliphatic and aromatic aldehydes and furfural.

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Received January 22, 1936.

Review

Physical Principles and Applications of Magneto-Chemistry. By Prof. S. S. Bhatnagar and Dr. K. N. Mathur, D.Sc. Published By Macmillan & Co., London, 1935. Pp. 375 + VXI. Price 21*s*. net.

The authors deserve congratulations on having brought out this volume, which deals in a comprehensive manner all the various aspects of the subject, both theoretical and experimental. The treatment is both intelligible and interesting.

Though the pioneering work of Perkin and Pascal on the relation between chemical constitution and magnetic properties of substances directed the attention of chemists to this branch of study, the subject did not attain its full significance and evoke an extensive interest till lately after the development of atomic structure.

In giving prominence to the chemical side, the authors have not ignored its physical aspect in the least, so as to present a connected and comprehensive account of the entire subject.

After a short historical account dealing with earlier theories of magnetism, fundamental ideas and terms have been defined, and an account of various magnetic measurements with special reference to susceptibility values has been given; various types of magnetic balances, including those by Prof. Bhatnagar and his co-workers, are fully discussed in this connection.

The chapter on "Pan-Magnetism", in which Pascal's work has been thoroughly reviewed, is followed by a chapter on "Spectroscopy and Atomic Structure" by way of introduction to the fundamental ideas of the modern theories of magnetism.

After dealing with the theories of diamagnetism, paramagnetism and ferromagnetism, the relation between magnetism and valency—a subject of great importance and interest to the chemists—is fittingly dealt with in a very comprehensive and detailed manner. The theories of Werner, Kossel, Lewis, Heitler and London, Sidgwick, Pauling and others are fully discussed in this connection. One notable feature of this work is its freedom from bias to any particular view, so that the reader may go through it with an open mind.

An account of various magneto-optical properties useful in chemical investigation, *e.g.*, Faraday-effect, Cotton-Mouton effect, Kerr-effect and Photo-magnetic effect, is given in Chapter X.

This is followed by chapters on various important magnetic effects of some significance in technology and engineering, on magne-crystallic action, and on the influence of magnetic fields on chemical reactions—a subject of special appeal to the chemists.

The last chapter deals with some physico-chemical applications of magnetic properties.

The book closes with an enumeration of some outstanding problems which stand in need of closer investigation and proper solution.

The values of various physical constants, and of magnetic susceptibilities of a large variety of substances, are added in the appendix. The list of references is fairly wide and quite up-to-date.

As Prof. Bhatnagar's own contribution to the development of the subject, specially in its chemical aspect, is not inconsiderable, the present volume is sure to prove of great value and service to all those who are interested in this branch of study.

The printing and get-up of the book leave nothing to be desired.

P. R.

Influence of Light on Some Biochemical Processes. By Prof. N. R. Dhar. Published by the Society of Biological Chemists, India, 1935. Pp. 73. Price Re. 1.

The small monograph contains two principal chapters (I) Influence of Light on Soil Processes, (II) Influence of Light on Plant Processes. It brings together within a small compass, the views and the experimental results scattered over numerous publications by the author.

In the first chapter, Prof. Dhar claims that in the soil, specially of the tropical countries, oxidative photo processes occur side by side with bacterial oxidation, and brings out a large mass of experimental data in support of the view that light markedly accelerates the oxidation of amino-acids to ammonia, of ammonium salts to nitrites and of nitrites to nitrates. The author has also made very serious attempts to substantiate the view that the carbon-nitrogen ratio in soils is not controlled by the energy requirements of the micro-organisms but is regulated by the ease with which proteins are oxidised by air and light in presence of carbonaceous substances, and arrives at the important conclusion that the preservation of soil nitrogen by addition of molasses is due to the diminution in the velocity of oxidation of nitrogenous compound.

Chapter II has been devoted to the discussion of the mechanism of assimilation and the synthesis *in vitro* of reducing sugars and amino-acids by light in presence of photocatalysts.

Prof. Dhar has succeeded in presenting many new conceptions to the serious attention of Physical chemists and Biochemists, and it is to be hoped that his future researches will place these views on unassailable foundations.

J.C. G.

Anorganisch Chemisches Praktikum. BY PROF. DR. WILHELM MANCHOT. PUBLISHED BY VERLAG VON THEODOR-STEINKOPFF—DRESDEN AND LEIPZIG—1935. Pp. 103 + VIII. PRICE RM 4·30.

This book is an embodiment of instructions imparted to the beginners in the Inorganic Laboratory of the Technische Hochschule of Munich, where, in the form of a manuscript, it has been in use for several years.

As mentioned by the author himself it is not a text-book, but an introduction to the performance of experiments by the students themselves in the practical class for the purpose of acquiring experimental skill, observation capacity and evidences for theoretical conceptions.

Fundamental principles and theories have been described briefly at places, where they have been found necessary for the elucidation of experimental facts.

The book is mainly a description of simple experiments to explain the properties of various elements and compounds. These experiments include all the important analytical reactions of the substances concerned.

In addition to all the commoner elements, lithium, molybdenum, tungsten and uranium have also found place in the book. A few important micro-reactions for certain elements have also been added under respective heads.

In its own way the book is well-written, but the reviewer is of opinion that there is nothing special in it to justify its recommendation for use in the Indian Universities.

P. R.

A Comparative Study of the Utility of the Milk and Ghees of the Indian Cow and Buffalo as Human Food Materials. BY PROF. N. N. GODBOLE AND SADO GOPAL, M.SC. OF BENARES HINDU UNIVERSITY. PP. 24. PRICE 4 AS.

Ghee in India is fat derived from the melting of butter. The author has tried to focus particularly our attention to the chemical compositions and food values of the two kinds of ghees and milk of cows and buffaloes rather than answer definitly which kinds are superior. Both the butter fats contain the vitamins A and D and both the types of milk are rich in vitamins A, D and E. Buffalo ghee is rich in vitamin D, whilst cow ghee is rich in vitamin A. Both types of milk are far short of the standard food ratio of carbohydrates, fat and albuminoid *i.e.*, 5:1:1. Buffalo ghee contains greater proportion of undigestible higher saturated acid glyceride but also greater proportion of digestible lower acids glyceride so that the author's statement that on the former account cow's ghee and for the matter of that, cow's milk should be held to be superior to those of buffalo must be taken with reserve especially in absence of strictly scientific comparative feed experiments. The author, *interalia*, has also discussed the composition of the milk of other mammals and shown that ass milk approaches the standard ratio mentioned above.

M. G.

Dictionare de la Chimie et de ses applications. EDITTED BY DRS. C. DUVAL, R. DUVAL AND R. DOLIQUE. PUBLISHED BY HERMANN & CO. 6, RUE DE LA SORBONNE, VI^{e} PARIS PP. 780. PRICE 90 FR.

The rapid advance of chemistry and the production of numerous types and varieties of compounds having peculiar specific names, is making the subject gradually abstruse to the workers in th field and hence a hand book of the type "Dictionare de la chimie et de ses applications" becomes a necessity to the chemists. The book has been very carefully written and although completeness is always impossible in this rapid growing branch of science, yet it can be safely recommended as a good collection of most of the specific names and formulae, with their uses.

M. G.

Behaviour of Gases under the Influence of High Frequency Discharge. Ammonia and Hydrogen.

By B. S. Srikantan.

Hiedmann (*Z. physikal. Chem.*, 1933, **A 164**, 20) observed that under the influence of high frequency discharge through hydrogen in degassed tubes of pyrex or silica, a condensible product which he thought to be silane, was obtained. Bhatt (a paper read in the Easter session of The South Indian Science Association, Bangalore 1934) contradicts this and shows that the product was water vapour. Bhatt worked with a 2 metres wave-length of high frequency magneton. In the case of hydrogen he reports a disappearance of hydrogen which could be recovered only to about 2/3 of the original quantity by degassing and baking out the tubes. In view of the above conflicting results it was thought interesting to publish the results of the present author, obtained as early as 1929.

FIG. 1.

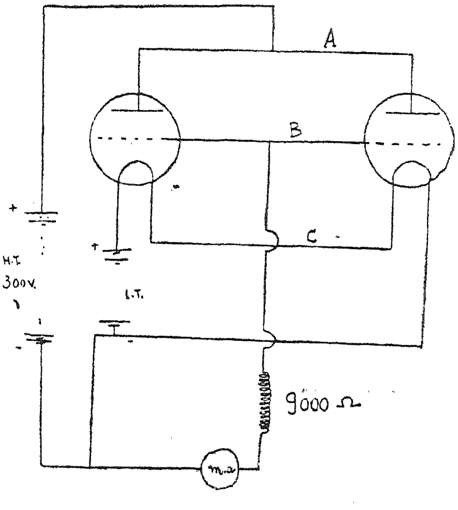
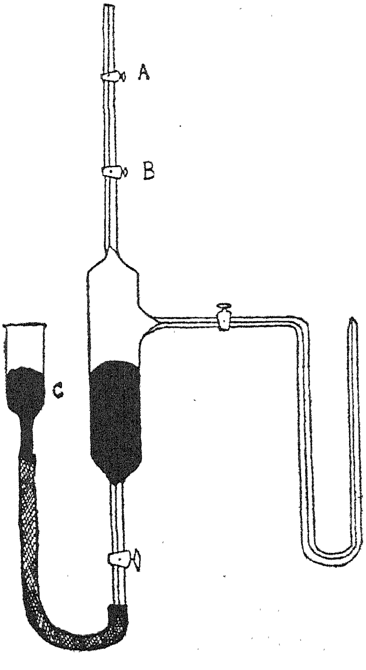


FIG. 2.



In an attempt to study the kinetics of the decomposition of ammonia at low pressures under the influence of electrode-less discharge by means of a high frequency oscillator, it was found that reproducible results could not be obtained due to some peculiar effect coming into play between the gas and the walls of the vessel. Hence the study of chemical reaction was abandoned and the behaviour of ammonia and hydrogen under the influence of the discharge was studied.

The High Frequency Oscillator.—Two LS_5 valves capable of carrying a filament current of 0·8 amp. each were connected up in parallel as shown in the diagram (Fig 1), with suitable inductances and chokes. The whole was mounted on a bakelite board with waxed pyrex glass tubes holding it in position on a well paraffined wooden base. The straight wires A, B, C, themselves formed the inductances. They were made of no. 20 copper wire, silver deposited. Extensive lecher wire measurements were made and though it was possible to get short waves of the order of 2 to 2·5 metres, vacuum tubes placed in the vicinity of the inductance could not be made to glow. Hence various types of inductances were tried. Those with the loops with ebonite separators proved useful in as much as the vacuum tube could be placed in the centre of the loop. One with two loops gave on lecher wire, waves of about 4·2 metres but discharge started with difficulty. Finally one with 4 loops was adopted since it was able to start a discharge in the vacuum tube placed at the centre, without any difficulty. The waves were of 10·5 metres in length and were used throughout the experiment. The reaction tube consisted of Pyrex tube 6″ long and $\frac{3}{4}$″ in internal diameter, closed at one end and connected to a system of pumps and manometer. The drying tube contained lumps of baryta for the elimination of moisture instead of the usual phosphorus pentoxide. Pressures were measured with the special types of Mecleod guage and Pirani gauge was specially avoided since it was thought that a hot filament in the system would induce other effects.

EXPERIMENTAL.

Preliminary.—Pure dry ammonia gas was led into the evacuated apparatus. According to the reaction $2NH_3 \rightarrow N_2 + 3H_2$, there ought to be only twice the amount of the original volume, even if complete decomposition had taken place. But however, a series of experiments showed that under action of the discharge some times, the amount of gas in the tube was far in excess of that demanded by the above equation. Starting with $9{\cdot}5 \times 10^{-2}$ mm. of ammonia with a discharge (plate current 40 m.a.) for 300 min. there was $39{\cdot}5 \times 10^{-2}$ mm. of gas in the apparatus. The apparatus was next thoroughly exhausted, at the same time baking out in an electric furnace. While still under evacuation, the discharge was sent in (36 m. a. plate current; 2·8 m. a. grid current) till there was a constant pressure in the apparatus to $0{\cdot}9 \times 10^{-2}$ mm. This time, when again starting with $9{\cdot}5 \times 10^{-2}$ mm. of ammonia under similar conditions, $85{\cdot}7 \times 10^{-2}$ mm. of gas accumulated even in 20 minutes.

The experiments were then conducted with hydrogen instead of ammonia. Starting with $19{\cdot}7 \times 10^{-2}$ mm. of hydrogen under similar conditions of discharge as before, the pressure rose to $24{\cdot}5 \times 10^{-2}$ mm. in two hours and remained steady thereafter. The apparatus was then exhausted to $0{\cdot}5 \times 10^{-2}$ mm. and the discharge continued as before. In about 30 minutes there was evolution of gas to $3{\cdot}1 \times 10^{-2}$ mm. where it remained steady.

It is possible from the above that the walls of the highly exhausted tube would rapidly adsorb the gases let in and during the action of the high frequency discharge would be liberated exactly as would happen during the degassing of the vacuum tubes by baking out. The easily condensible and basic nature of ammonia would exhibit this behaviour to a more marked degree than hydrogen.

In order to test this idea, the exact amount of gas let in at a known pressure, and the volume of the apparatus including dead-space leads to pumps, etc., has to be known.

Calibration of the volume of the apparatus (including the dead space leads to pumps, etc).—A micro-burette with a levelling bulb as shown in Fig. 2. was attached to the apparatus. The volume of the capillary between the taps A and B including the capillary space in tap A was carefully calibrated. It was 0·0361 c.c. For the calibration of the volume of the whole apparatus nitrogen was taken as the reference gas. The apparatus was evacuated moderately and known volumes of nitrogen gas, as measured by the micro burette at atmospheric pressure, was let into the apparatus. From the reading of the Mecleod gauge, the volume of the apparatus was calculated. Care was taken not to exhaust the apparatus too hard lest there should be adsorption of the gas by the evacuated walls of the vessel. A few results of the calibration are given in Table I.

TABLE I.

Initial pressure in apparatus.	Amount of gas introduced at atmospheric pressure.	Final pressure in apparatus.	Volume of apparatus.
0·95 mm. $\times 10^{-2}$	0·0361 c.c.	7·56 mm. $\times 10^{-2}$	368·5
12·20	0·0361	19·44	337·0
31·00	0·1083	53·05	334·0
53·05	0·1083	75·17	335·0

The first result in this table shows a higher value since due to evacuation to a low degree, some gas must have gone into the walls of the vessels. The mean volume of the apparatus was taken as 335 c.c.

Experiments with Ammonia.

0·1083 C.c. pure dry ammonia at 669·6 mm. pressure were let into the apparatus which was evacuated previously to a pressure of $0{\cdot}58 \times 10^{-2}$ mm. The Mecleod gauge showed only a pressure of $2{\cdot}0 \times 10^{-2}$ mm. whereas the calculated pressure ought to have been $21{\cdot}66 \times 10^{-2}$mm. So nearly 90% of ammonia have been adsorbed by the walls of the vessel.

With a discharge (plate current 37 m.a. and grid current 2·3 m.a.) in 2 minutes, a further quantity was adsorbed and pressure fell to $0{\cdot}71 \times 10^{-2}$ mm. and remained steady thereafter. Again a further quantity of ammonia was introduced into the apparatus till the pressure was $6{\cdot}5 \times 10^{-2}$ mm. and the fall of pressure in presence of the discharge is shown in Table II.

TABLE II.

Surface of glass saturated previously with ammonia.

Time (min.) ...	0·0	0·5	30·0	70·0	100·0	160·0
Pressure (mm. $\times 10^{-2}$) ...	6·5	12·4	0·78	2·08	3·56	3·56

The above result with ammonia is capable of being almost exactly reproducible. The excess amount of ammonia is not adsorbed since the surface is already saturated with ammonia. Results in Table II suggest that the instant the discharge was started there has been a sudden decomposition of ammonia giving a pressure of the resulting gas of $12{\cdot}4 \times 10^{-2}$ mm. In 30 minutes in the discharge, the whole of this nitrogen and hydrogen are adsorbed by the surface which is still free from these gases, leaving again an amount of ammonia of the order of $0{\cdot}78 \times 10^{-2}$ mm. in equilibrium with that adsorbed on the surface, before the experiment. A further continuation of the discharge expelled the nitrogen which is the least adsorbed on the surface in comparison with ammonia and hydrogen. In the above experiment it is evident that $5{\cdot}79 \times 10^{-2}$ mm. of ammonia decomposed under the influence of the discharge giving $11{\cdot}69 \times 10^{-2}$ mm. of a mixture of nitrogen and hydrogen, and after adsorption of hydrogen, left a residue of $2{\cdot}85 \times 10^{-2}$ mm. of nitrogen. This is in accordance with the stoicheometric equation for the decomposition of ammonia. In the absence of spectroscopic evidence as to the nature of the residual gas this conclusion appears plausible.

Experiments with Hydrogen.

The tube was thoroughly baked out under prolonged exhaustion and the apparatus was washed several times with hydrogen thereafter. Finally the apparatus was evacuated to a pressure of $0{\cdot}19 \times 10^{-2}$ mm. 0·0722 C.c. of hydrogen at 669·9 mm.pressure was introduced in the apparatus. The Mecleod gauge showed a pressure of $14{\cdot}34 \times 10^{-2}$ mm. The calculated pressure is $14{\cdot}44 \times 10^{-2}$ mm. The following table records the effect of the discharge.

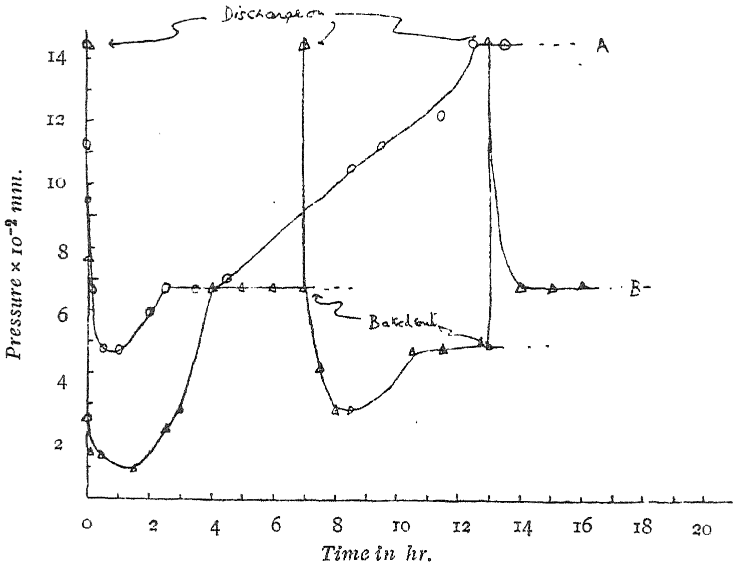
TABLE III.

Plate current = 45 m.a. Grid current = 5 m.a.

Time.	Pressure.	Time.	Pressure.
0·0 min.	14·34 mm. × 10^{-2}	270·0 min.	2·83 mm. × 10^{-2}
30·0	1·39	390·0	8·69
90·0	0·90	510·0	9·30
150·0	1·89	630·0	9·30
210·0	2·13		

At this stage when about $\frac{2}{3}$ of the original gas was desorbed under the prolonged influence of the discharge, the tube was baked out at about 400° for two hours. The apparatus was cooled and the pressure inside was $14{\cdot}44 \times 10^{-2}$ mm. The original quantity of the gas was recovered. On subjecting it again to the high frequency discharge, the results in Table III could be repeated again. So hydrogen disappears almost completely under the influence of the discharge but in about 10 hours working, about 2/3 of the original amount could be degassed. The whole amount is obtained by baking out the tube. This precludes the possibility of any new gas being formed.

FIG. 3.



The data presented in Fig. 3 are obtained from experiments conducted with 0·0722 c.c. of gas at 670·55 mm. at a pressure of $14{\cdot}44 \times 10^{-2}$ mm. in the apparatus. Curve A shows that the hydrogen is rapidly adsorbed in the first 30 minutes, the pressure falls to a low value of $4{\cdot}75 \times 10^{-2}$ mm. after which degassing begins and goes on steadily except for a slight fatigue when $6{\cdot}73 \times 10^{-2}$ mm. are reached and after which at the end of 14 hours the whole of the hydrogen is recovered. The graph shows that the initial drop is far lower when the apparatus is previously heated under vaccuum than otherwise. The fatigue during degassing is obtained again at a pressure of $6{\cdot}75 \times 10^{-2}$ mm. If the tube is baked out at 400°, the original amount of gas is expelled. The process of adsorption and desorption can again be repeated in the presence of the high frequency discharge. The existence of a stop during degassing at $6{\cdot}73 \times 10^{-2}$ mm. cannot be explained without further investigation.

CONCLUSIONS.

From the foregoing experiments the following conclusions have been drawn.

1. Ammonia is greatly adsorbed by the walls of highly evacuated glass tubes as compared with hydrogen.

2. When the walls of the vessel are saturated with reference to ammonia, the extra gas put in decomposes at once into nitrogen and hydrogen. In the presence of the discharge the hydrogen is adsorbed leaving off nitrogen.

3. The adsorption of ammonia appears to be irreversible under the influence of the electrodeless discharge, but hydrogen could be adsorbed as well as desorbed from the surface in a quantitative manner by the discharge.

4. The adsorption of hydrogen under the influence of the discharge is like the degassing of the tube by baking at 400°. In both the cases the whole of the gas put in could be recovered back.

5. In no case was obtained more gas than was put in. The possibility of any new gas formation seems to be remote.

This work was done in the Indian Institute of Science, Bangalore and the author's best thanks are due to Prof. H. E. Watson for his keen interest in this work.

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Received November 11, 1935.

Formation of Heterocyclic Compounds from Thioacetylcarbamic Acid Derivatives. Part I.

By Tejendra Nath Ghosh.

This paper describes experiments on the action of hydrazines and diamines on dicarbethoxythioacetylcarbamic acid (A), carbethoxyacetothioacetylcarbamic acid (B) and diacetylthioacetocarbamic acid (C) (*J. Indian Inst. Sci.*, 1933, 16A, 107).

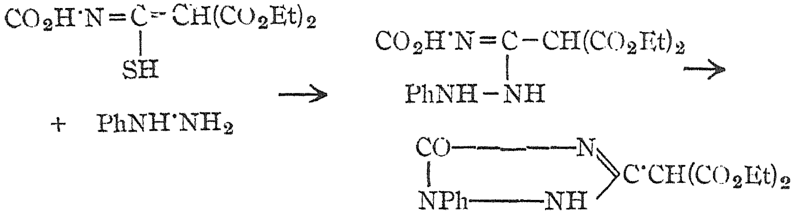
$CO_2H\cdot NH\cdot CS\cdot CH\,(CO_2Et)_2$ (A)

$CO_2H\cdot NH\cdot CS\cdot CH\,(CO_2Et)\cdot CO\cdot CH_3$ (B)

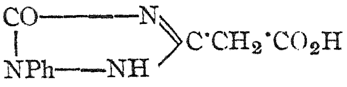
$CO_2H\cdot NH\cdot CS\cdot CH\,(CO\cdot CH_3)_2$ (C)

The above compounds which bear a close resemblance to acetylurethane react readily in the cold with amines and hydrazines with evolution of sulphuretted hydrogen. The fact that these compounds are much more reactive towards basic compounds than acetylurethane (*cf.* Ghosh and Betrabet, *J. Indian Chem. Soc.*, 1930, 7, 899) is explained on the basis that sulphur is more acidic than oxygen, as is evinced by a comparison of the mercaptans with the alcohols. In this connection reference is made to the great reactivity of thioketonic esters (Mitra, *J. Indian Chem. Soc.*, 1931, 8, 472).

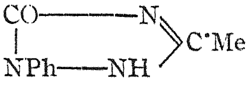
An 1 : 2 : 4-triazole derivative (I) is obtained by reacting the compound (A) with phenylhydrazine, the reaction taking the following course :



(I)



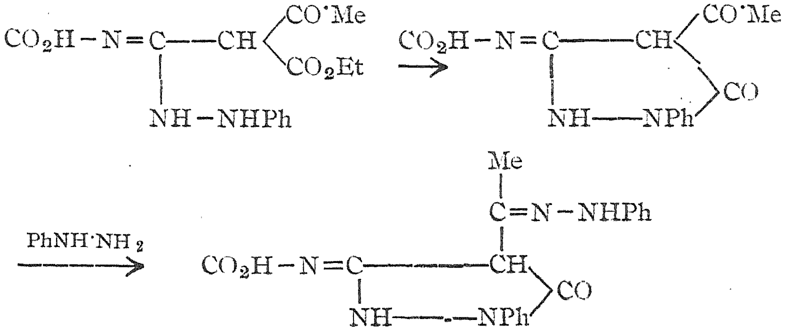
(II)



(III)

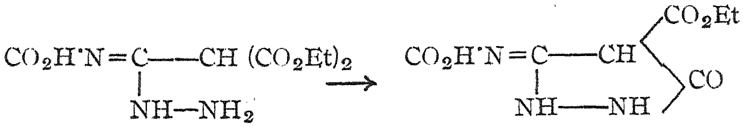
The formula assigned to (I) is established by the analytical data and by the fact that the compound is insoluble in cold alkali and does not decolourise bromine water. On hydrolysis it yields the mono-acid (II) which, on decarboxylation, yields the compound (III). In this connection reference may be made to the work of Ghosh and Betrabet (*loc. cit.*) on the synthesis of 1 : 2 : 4-triazole derivatives from acetylurethane and hydrazines.

The compound (B) reacts with phenylhydrazine to yield a pyrazolone derivative (IV). That the carboxyl group in this compound is firmly attached to the nitrogen atom is shown by the fact that carbon dioxide is not eliminated by heating the compound with even 10 % alcoholic potash.

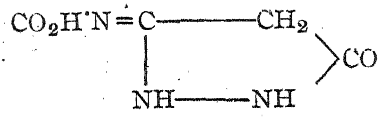


(IV)

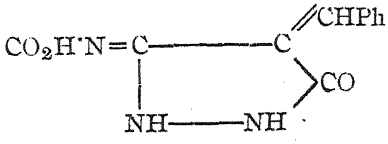
With hydrazine hydrate the compound (A) yields a pyrazolone derivative (V) (*cf.* Worrall, *J. Amer. Chem. Soc.*, 1923, **45**, 3092, on the action of hydrazine hydrate on dicarbethoxythioacetanilide) which, on hydrolysis, yields the mono-acid (VI). The compound (VI) is stable towards alkali and reacts with benzaldehyde to give the compound (VII), confirming thereby the presence of an active methylene group.



(V)

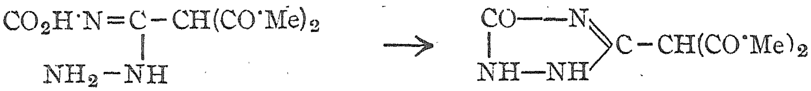


(VI)

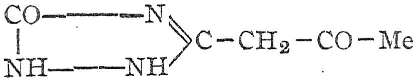


(VII)

The compound (C), unlike (A), gives with hydrazine hydrate not a pyrazolone but a triazole derivative (VIII) which is hydrolysed by alkali to yield the compound (IX).

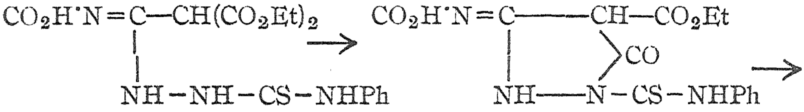


(VIII)

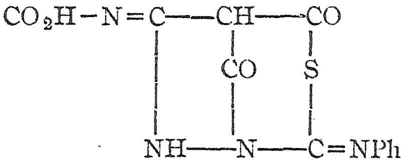


(IX)

4-Phenylthiosemicarbazide and the compound (A) react to form a thioheptadiazine derivative (X), (Xa) being postulated as an intermediate (*cf.* De, *J. Indian Chem. Soc.*, 1926, **3**, 31; Ghosh and Betrabet, *loc. cit.*). The compound (X) is not desulphurised by mercuric oxide indicating that the sulphur atom is cyclic; with acetic anhydride it decomposes into phenyl *iso*thiocyanate and a tarry product.

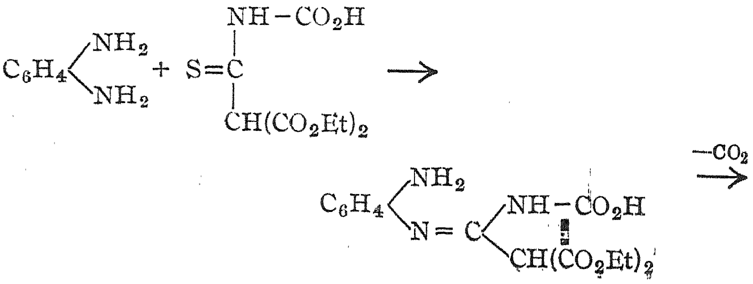


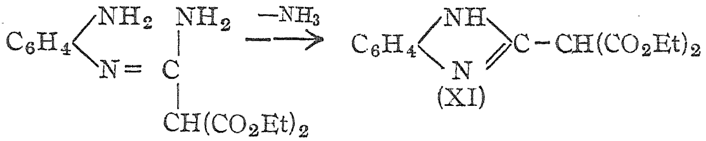
(X*a*)



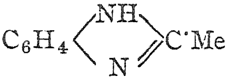
(X)

The compound (A) reacts with *o*-phenylene diamine to yield a benzimidazole derivative (XI), the reaction taking the following course.



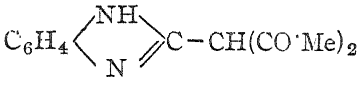
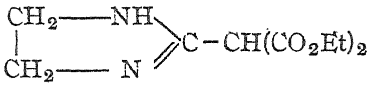


(XI)



(XII)

On hydrolysis the compound (XI) yields 2-methylbenzimidazole (XII) (Hübner, *Annalen*, 1881, **209**, 353); this reaction confirms the assigned constitution. The compound (C) with *o*-phenylenediamine gives similarly the benzimidazole derivative (XIII) and the compound (A) likewise with ethylenediamine gives the imidazole derivative (XIV).



(XIII) (XIV)

In connection with the synthesis of imidazole derivatives, mention should be made that many substances containing the imidazole group are formed in the metabolic processes of the living organism. Histamine (β-iminazoylethylamine) possesses pronounced physiological activity.

From the reactions studied above, it is observed that thioacetylcarbamic acid derivatives are characterised by their pronounced reactivity and as such are of considerable value for synthetic purposes. The general mechanism of the above reactions is that sulphuretted hydrogen is first eliminated and then ring-closure is effected by the elimination of either alcohol or water.

EXPERIMENTAL.

Dicarbethoxythioacetylcarbamic acid (A), *Carbethoxyacetothioacetylcarbamic acid* (B) *and Diacetylthioacetocarbamic acid* (C) were prepared according to the method of Ghosh and Guha (*J. Indian Inst. Sci.*, 1933, **16A**, 111).

3-Keto-2-phenyl-5-dicarbethoxymethyl-dihydro-1:2:4-triazole (I).—Phenylhydrazine (2·2 g.) was added to an alcoholic solution of the compound (A) (5·3 g.) when the reaction immediately commenced with evolution of sulphuretted hydrogen and rise in temperature. For completion of the reaction, the reaction mixture was heated under reflux for about an hour and on cooling, a crystalline solid was obtained which crystallised from alcohol in colourless shining rectangular plates, m.p. 203°, yield 3 g. (Found: C, 56·11; H, 5·75; N, 12·98. $C_{15}H_{17}O_5N_3$ requires C, 56·42; H, 5·33; N, 13·17 per cent). It does not decolourise bromine water and is insoluble in cold dilute alkali.

3-Keto-2-phenyl-dihydro-1:2:4-triazole-5-acetic acid (II).—The above compound (I, 2 g.) was heated on the water-bath with excess of 15% alcoholic potash for about 5 hours, when the alcohol was distilled under reduced pressure. The dried mass was treated with cold water and acidified slowly with acetic acid when there was evolution of carbon dioxide. The solid was purified by dissolving in aqueous bicarbonate and acidification with acetic acid. The product was crystallised from alcohol in colourless rectangular plates, m.p. above 300° (turning dark at 280°), yield 0·8 g. (Found: N, 19·01 $C_{10}H_9O_3N_3$ requires, N, 19·17 per cent).

2-Phenyl-3-keto-5-methyldihydro-1:2:4-triazole (III).—The above compound (II) was heated on the water-bath with excess of 20% aqueous potash for 7-8 hours. The solution was cooled and acidified with acetic acid when there was evolution of carbon dioxide. The solid was crystallised from alcohol in brownish white needles, m.p. 210-212° (decomp). It is soluble in hydrochloric acid and precipitated by aqueous bicarbonate. (Found: N, 23·81. $C_9H_9ON_3$ requires N, 24·00 per cent).

2- Carboxyimino - 4 - acetylphenylhydrazone - 1 - phenylpyrazolone (IV).—The method of preparation is as with (I). The reaction product crystallised from hot water in colourless needles, m.p. 185-86° (decomp.). (Found: C, 61·25; H, 5·28; N, 19·95; M.W. by titration, 356. $C_{18}H_{17}O_3N_5$ requires C, 61·54; H, 4·84; N, 19·94 per cent. M.W., 351). It is readily soluble in bicarbonate solution and precipitated by acids. It does not give any azo-compound with ferric chloride and does not decolourise bromine water.

3-Carboxyimino-4-carbethoxypyrazolone (V).—The method of preparation is as with (I). The product was purified by precipitation by acid from its solution in sodium bicarbonate and finally crystallised from dilute alcohol in beautiful colourless needles, m.p. 181°. [Found: N, 17·32; 17·34; H_2O, 10·78; M.W. (by titration), 240. $C_7H_9O_5N_3$, $1\frac{1}{2}H_2O$ requires N, 17·35; H_2O, 11·15 per cent. M.W., 242]. It does not yield any azo-compound with ferric chloride. When heated at its melting point for about 2 hours, it lost the water of crystallisation which was estimated.

3-*Carboxyiminopyrazolone* (VI).—The above compound (V, 3 g.) was treated with excess of 10% alcoholic potash and the clear solution heated on the water-bath for about half an hour when a voluminous precipitate slowly came out, which was kept overnight at room temperature. It was filtered, washed several times with alcohol and treated with dilute acetic acid when there was evolution of carbon dioxide. The clear solution was evaporated to dryness and the dried mass dissolved in cold water, when the brown solution, on standing for some time, gave a crystalline precipitate which further crystallised from water in brownish white prisms, m.p. above 300° (turning dark at 250°), yield 1 g. (Found: N, 23·41; M. W. by titration, 178. $C_4H_5O_3N_3$, $2H_2O$ requires N, 23·46 per cent. M. W., 179).

3-*Carboxyimino-4-benzylidene-pyrazolone* (VII).—An acetic acid solution of the above compound (VI, 1·8 g.) and benzaldehyde (1·1 g.) was heated under reflux for about an hour and diluted with water. The precipitated solid crystallised from dilute acetic acid in colourless rectangular plates. It softens and turns pink at 180° and slowly resinifies above 280°, yield 1·4 g. It is readily soluble in aqueous bicarbonate. (Found : N, 16·12. $C_{11}H_9O_3N_3$, $2H_2O$ requires N, 15·73 per cent).

3-*Keto-5-diacetylmethyl-dihydro-1:2:4-triazole* (VIII).—The method of preparation is as with (I). The reaction mixture was diluted with water until the solution was slightly turbid. On being allowed to cool slowly, the solution deposited a crystalline mass which crystallised from hot water in colourless slender needles, m. p. 70-71°. (Found : C, 45·62 ; H, 5·28 ; N, 22·68. $C_7H_9O_3N_3$ requires C, 45·90 ;H, 4·91; N, 22·95 per cent). It is insoluble in aqueous bicarbonate but readily soluble in alkali. It gives a red colouration with ferric chloride.

3-*Keto-5-acetylmethyl-dihydro-1:2:4-triazole* (IX).—The method of preparation is as with (II). The solid crystallised from dilute alcohol in colourless needles, m. p. 228-230°. (Found : N, 30·05.

$C_5H_7O_2N_3$ requires N, 29·78 per cent). It is insoluble in aqueous bicarbonate but readily soluble in alkali.

Dicarbethoxythioacetylcarbamic acid and 4-phenylthiosemicarbazide : Formation of 3-carboxyimino-5-keto-7-phenylimino-1:4-carbonyl-1:2:6-thioheptadiazine (X).—The method of procedure is the same as in the case of the previous compound (I). The reaction product crystallised from alcohol in colourless plates, m. p. 183° (decomp.). [Found: N, 18·44 ; S, 10·35 ; M. W. (by titration), 301. $C_{12}H_8O_4N_4S$ requires N, 18·42 ; S, 10·52 per cent. M. W., 304]. It is not desulphurised by yellow oxide of mercury. It is soluble in bicarbonate solution and in moderately strong hydrochloric acid. It does not give any azo-compound with ferric chloride.

2-*Dicarbethoxymethyl-benzimidazole* (XI).—A glacial acetic acid solution of equimolecular proportions of *o*-phenylenediamine and dicarbethoxythioacetylcarbamic acid was heated under reflux till the evolution of sulphuretted hydrogen had ceased. On cooling, a crystalline mass at once came out which crystallised from glacial acetic acid in colourless slender needles, m. p. 218°. (Found : N, 10·28. $C_{14}H_{16}O_4N_2$ requires N, 10·14 per cent). It is insoluble in alkali but soluble in concentrated hydrochloric acid. It does not respond to diazotisation and coupling with β-naphthol.

Hydrolysis of compound (XI) : *Formation of 2-methylbenzimidazole* (XII).—A mixture of the above compound (5 g.) and 15% alcoholic potash (40 c. c.) was heated under reflux on the water-bath for about 5 hours and the solution was evaporated nearly to dryness on a water-bath. The aqueous solution of the pasty mass was acidified with acetic acid and evaporated to dryness. The dried mass was finely powdered and triturated with cold water, when an insoluble white powder was obtained which crystallised from hot water in colourless needles, m. p. 169-70° (mixed m. p. with 2-methyl-benzimidazole, Hübner, *loc. cit.*), yield 0·8 g. (Found : N, 21·42. $C_8H_8N_2$ requires N, 21·21 per cent).

2-*Diacetylmethyl-benzimidazole* (XIII).—An alcoholic solution of equimolecular proportions of *o*-phenylenediamine and diacetylthioacetocarbamic acid was heated under reflux till the evolution of sulphuretted hydrogen had ceased. The solution was cooled and diluted with water when a viscous semi-solid mass was obtained. It was purified by dissolving in alcohol and precipitation by adding large quantity of ether. The solid was finally crystallised from a mixture of alcohol and ether in colourless needles, m.p. 138-39°. (Found: C, 66·89; H, 6·01. N, 13·19. $C_{12}H_{12}O_2N_2$ requires C, 66·66; H, 5·55; N, 12·96 per cent). It does not condense with phenyl *iso*cyanate, showing thereby the absence of any free amino group.

The *hydrochloride* was obtained by dissolving the above compound in hydrochloric acid and evaporating the solution. The solid crystallised from water acidulated with a few drops of hydrochloric acid in colourless shining rectangular plates, m. p. 243-244° (decomp.; producing a fine green colouration). (Found: N, 10·73. $C_{12}H_{12}O_2N_2$, HCl requires N, 11·11 per cent). On treatment with aqueous bicarbonate, it yielded the original compound (XIV).

2-*Dicarbethoxymethyl-dihydro-imidazole* (XIV).—The method of preparation is as with (XI). The product crystallised from water in colourless slender needles, m. p. 100-101°. It is soluble in cold dilute hydrochloric acid and precipitated by alkali. It does not condense with phenyl *iso*cyanate, showing thereby the absence of any free amino group. (Found: N, 12·41. $C_{10}H_{16}O_4N_2$ requires N, 12·28 per cent).

My grateful thanks are due to Professor P. C. Guha, D.Sc., for his kind interest in this investigation.

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Dyes Derived from Acenaphthenequinone. Part V. 2-(6-Methyl)-thionaphthene-acenaphthylene-indigos.

By Sisir Kumar Guha.

Martinet (*Rev. Gen. Mat. Col.*, 1921, **25**, 17)* has formulated a rule that the effect of the two auxochromes in *para* position (5:5′) is cumulative and when in *meta* position (6:6′) with respect to one another they act in contrary direction. This rule is particularly well exemplified in the indigoid series. It has been found that all 5:5′ derivatives are decidedly deeper in colour than the corresponding 6:6′ derivativies. The substituents may be C_2H_5S, C_2H_5O, Halogen, CH_3, NH_2, OH etc., (*cf.* Rowe, "Colour Index," 1924 Ed., Nos. 1216, 1217, 1209, 1210, 1208, 1182, 1248, 1193; Auwers and Arndt, *Ber.*, 1909, **42**, 541; D.R.P. 204763, Friedlander, 9, 589; G. P. 239673, 240805, Viles, *J.S.D.C.*, 1914, **30**, 25, etc.).

In the present investigation, indigoid dyes have been obtained from acenaphthenequinone, 3-chloro-, 3-bromo-, and its 1-methoxy derivative and 6-methyl-3-hydroxy-thionaphthene (Friedlander, *loc. cit.*; Auwers and Thies, *Ber.*, 1920, **53**, 2293) with the object of studying the effect, if any, produced on the colour of 2-thionaphthene-acenaphthylene-indigo, commercially known as Ciba scarlet-G (Bezdzik and Friedlander, *Monatsh.*, 1908, **29**, 386; E.P. 344/08, G.P. 205377) and its various derivatives (Guha, *J. Indian Chem. Soc.*, 1932, **9**, 423) by the introduction of CH_3 group in the 6-position of the thionaphthene nucleus and how far this effect can be compared with 2-(5-methyl) thionaphthene-acenaphthylene indigos (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 679) and thus to see if the rule of Martinet is applicable to 2-thionaphthene-acenaphthylene-indigos as far as one methyl group in the thionaphthene part of the molecule is concerned.

The indigoid dyes described here are all sparingly soluble in alcohol and all of them dissolve in strong sulphuric acid giving deep green solutions from which the substances are reprecipitated by the addition of water in the form of flocculent precipitate, suitable for dyeing on wool from an acid bath. When strongly heated above the melting points, the dyes behave similarly to the corresponding 5-methyl derivatives (Guha, *loc. cit.*). The parent substance, its chloro- and bromo- derivatives are reduced by alkaline hydrosulphite giving violet blue, and blue vat from which dyes are regenerated on cotton by air. But the methoxy derivatives offered considerable resistance to reduction ; after prolonged treatment, the faint violet vat obtained in this case, turned by atmospheric oxygen into faint pink only [*cf.* 2-thionaphthene-8′-(1′-methoxy)-acenaphthylene-indigo and its 5-methyl derivative, Staudinger, Goldstein and Schlenker, *Helv., Chim. Acta*, 1921, **4**, 342; Guha, *loc. cit.*).

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* The paper is available to me in the form of an abstract only (*J. Chem. Soc.*, 1921, *i*, 273).

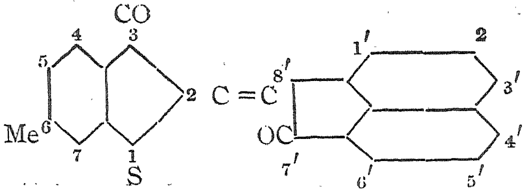
All these indigoid dyes are distinctly lighter in colour than those of the corresponding 5-methyl compounds (Guha, *loc. cit.*). A comparison of the colours of the dyeing on wool and on cotton of the compounds mentioned here with those obtained from the corresponding 5-methyl derivatives is given below. The substances are arranged, in both the series, according to the gradual increase of the shades of dyes developed on cloth and on wool.

Name of the compounds.	Dyeing shades	
	on wool.	on cotton.
2-(6- Methyl) - thionaphthene - acenaphthylene indigo	Vermillion	Vermillion
2-(5- Methyl) - thionaphthene - acenaphthylene indigo	Scarlet red	Scarlet red
2-(6-Methyl)-thionaphthene-8′- (3′- chloro) - acenaphthylene indigo	Vermillion	Vermillion
2-(5-Methyl)-thionaphthene-8′- (3′- chloro) - acenaphthylene indigo	Bright scarlet red	Deep scarlet red
2-(6-Methyl)-thionaphthene-8′- (3′- bromo) - acenaphthylene indigo	Bright vermillion	Light red
2-(5-Methyl)-thionaphthene-8′- (3′- bromo) - acenaphthylene indigo	Deep scarlet red	Deep scarlet red
2-(6-Methyl)-thionaphthene-8′-(1′-methoxy)-acenaphthylene indigo	Deep red	Faint pink
2-(5-Methyl)-thionaphthene-8′-(1′-methoxy)-acenaphthylene indigo	Deep red	Pink

Further studies in 2-thionaphthene-acenaphthylene-indigos having CH_3 group in 4-position of the thionaphthene nucleus are in progress.

EXPERIMENTAL.

2-(6-Methyl)-thionaphthene-acenaphthylene-indigo.



The solutions of acenaphthenequinone (0·455 g.) in boiling glacial acetic acid (80 c.c.) and 6-methyl-3-hydroxythionaphthene (0·41 g.) in boiling glacial acetic acid (20 c.c.) were treated with strong hydrochloric acid (6 c.c.) and shaken when vermillion coloured needle shaped voluminous crystalline precipitate immediately separated out. The mixture was heated to boiling for 15 minutes and filtered hot, washed with acetic acid and hot water. It was purified by boiling with alcohol and finally crystallised from glacial acetic acid or xylene in clusters of needles, m.p. 305°. The dye is soluble in chloroform, amyl alcohol, benzene, xylene, nitrobenzene, aniline, pyridine; difficultly soluble in carbon tetrachloride, glacial acetic acid; sparingly soluble in acetone and alcohol. It dyes cotton in vermillion shade from a deep violet blue (almost blue) vat obtained by the action of alkaline hydrosulphite and wool in the same colour from an acid bath. (Found: S, 9·38. $C_{21}H_{12}O_2S$ requires S, 9·75 per cent).

2-(6-*Methyl)-thionaphthene-8′-(3′-chloro) -acenaphthylene-indigo.*—3-Chloroacenaphthenequinone (0·866 g.) and 6-methyl-3-hydroxythionaphthene (0·656 g.) in hot glacial acetic acid (95 c.c.) were treated with concentrated hydrochloric acid (3 c.c.). The condensation product crystallised in fibre-like vermillion needles which were purified as the preceding compound and crystallised from pyridine or xylene in clusters of needles, m.p. 297°. It dyes wool in vermillion shade from an acid bath and cotton in the same shade from the blue vat obtained by alkaline hydrosulphite. It is difficultly soluble in benzene and amyl alcohol and the other properties resembie those of the preceding compound. (Found: Cl, 9·59. $C_{21}H_{11}O_2ClS$ requires Cl, 9·79 per cent).

2-(6-*Methyl)-thionaphthene-8′-(3′-bromo)-acenaphthylene-indigo* was obtained in the same way as the two foregoing compounds by the condensation of 3-bromoacenaphthenequinone (1·044 g.) and 6-methyl-3-hydroxythionaphthene (0·656 g.) in presence of 105 c.c. of hot glacial acetic acid and 3 c.c. of concentrated hydrochloric acid. The silky, bright, vermillion coloured crystalline product, after being boiled with alcohol, was crystallised from xylene in fine long rectangles, m.p. 302°. It dyes wool in bright vermillion shade from an acid bath and it dyes cotton in light red shade from the blue vat, formed by the action of alkaline hydrosulphite, although not so readily obtained as in the case of the mother compound and its chloro derivative. It resembles the chloro compound in its other properties. (Found : Br, 19·34. $C_{21}H_{11}O_2BrS$ requires Br, 19·65 per cent).

2-(6-*Methyl*)-*thionaphthene*-8′-(1′-*methoxy*)-*acenaphthylene-indigo*.—The deep brownish red hot solution of β-methoxyacenaphthenequinone (0·636 g.) and the methylhydroxythionaphthene (0·492 g.) in 115 c.c. of glacial acetic acid on treatment with 10 c.c. of concentrated hydrochloric acid immediately turned deep violet red (almost black) which on shaking deposited at once scarlet red sharp needle-shaped crystals. The whole of the mixture was boiled for 30 minutes, filtered hot, washed with acetic acid and hot water. It was found difficult to purify the substance by heating successively with alcohol and acetic acid to remove minute traces of the unreacted diketone. It was crystallised from pyridine, washed with dilute hydrochloric acid and hot water. It melts at 300° (softening at 298°). It dyes wool in deep red shades from an acid bath and cotton in faint pink colour from an alkaline hydrosulphite faint violet vat. It resembles the mother compound in this series in solubility. (Found : S, 9·1. $C_{22}H_{14}O_3S$ requires S, 8·93 per cent).

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Received December 12, 1935.

Dyes Derived from Acetylene Dicarboxylic Acid.

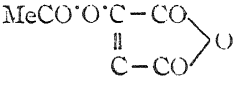
BY RAM NATH MISRA AND SIKHIBHUSHAN DUTT.

In the light of 'A theory of colour on the basis of molecular strain' advanced by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **129**, 1171; *J. Indian Chem. Soc.*, 1927, **4**, 99), substances containing acetylenic linkages should produce greater absorption of light in the higher wave lengths and consequently should be more deeply coloured than those containing ethylenic linkages by virtue of the former possessing triple bonds in place of the double bonds of the latter. A comparison of the absorption maxima of some well known ethylenic and acetylenic compounds brings out this fact very clearly. Thus:

Name of the compound.	Absorption maxima.	Name.	Absorption maxima.
Ethylene	2440	Elaidic acid	2500
Acetylene	2470	Stearolic acid	2640
Styrene	2730	Diphenyldiethylene	3400
Phenylacetylene	2740	Diphenyldiacetylene	3630
Cinnamic acid	2800	Diiodo-ethylene	2860
Phenylpropiolic acid	2820	Diiodo-acetylene	2940
Stilbene	2860		
Tolane	3030		

All the compounds mentioned above being colourless, their absorption bands lie in the ultra-violet region of the spectrum. Consequently their determination is a matter of considerable difficulty, and their position is also found to change slightly with change in conditions and solvents in which they are examined. On account of this it was thought that if some dyestuffs could be prepared containing acetylenic linkages in their molecules, they could be easily compared with their ethylenic analogues by direct determination of their absorption spectra by means of a high dispersion glass spectrograph either by eye observation or by photographic methods. Selection of an appropriate starting material was not particularly easy on account of the great paucity of data available in literature with regard to acetylenic compounds and acetylene dicarboxylic acid was selected for this purpose.

Acetylene dicarboxylic acid is very unstable in the ordinary sense, since when heated to its temperature of fusion, *i.e.*, 178°, it loses carbon dioxide progressively and gets converted first into propargylic acid and finally into acetylene. It does not give any anhydride under ordinary conditions, since most of the inorganic dehydrating agents like sulphuric acid, zinc chloride, hydrogen chloride, etc., employed for the production of anhydrides from dibasic acids, decompose it into carbon dioxide and propargylic acid. By heating with acetic anhydride, the acid gets converted into acetoxy-maleic anhydride (I). Acetyl chloride also gives the same product under identical conditions.



$$\begin{array}{l} \mathrm{MeCO{\cdot}O{\cdot}C-CO} \\ \qquad\qquad\ \ \| \qquad\quad \rangle\mathrm{O} \\ \qquad\qquad\ \mathrm{C-CO} \end{array}$$

(I)

Since the acid does not form an anhydride under the usual conditions, it was at first thought that the production of the pyronine dyestuffs from the acid, which require the intermediate formation of the anhydride, would not be feasible, but as the result of trial experiments it was found that pyronine dyestuffs are quite readily formed from acetylene dicarboxylic acid by condensation with aromatic amino and hydroxy compounds in the normal manner. Consequently the only hypothesis that can be advanced to explain this interesting phenomenon is that acetylene dicarboxylic acid does form an anhydride like maleic and succinic acids, but under ordinary conditions, the anhydride is very unstable and undergoes decomposition as soon as it is formed. If, however, substances are simultaneously present with which the anhydride can undergo condensation, it reacts with them as soon as it is formed with production of stable condensation products.

By analogy with dyes derived from citraconic acid (Dhar and Dutt, *J. Indian Chem. Soc.*, 1927, 4, 254) it is found that dyes derived from acetylene dicarboxylic acid also possess the same skeleton structure with the exception that the latter possess a triple bond in place of the double bond of the former. Consequently it can be expected that dyes derived from acetylene dicarboxylic acid will be more deeply coloured than the corresponding dyes derived from citraconic acid. This expectation with regard to these dyestuffs has been realised and on systemmatic comparison it has been found that they are more deeply coloured and more absorptive than the corresponding dyes derived from citraconic, itaconic or maleic acid. This will be quite evident from the tables of absorption maxima given at the end of the paper.

The following aromatic amino and hydroxy compounds have been condensed with acetylene dicarboxylic acid and the corresponding dyestuffs obtained: phenol, resorcinol, phloroglucinol, orcinol, *m*-dimethylamidophenol, *m*-diethylamidophenol and *m*-phenylenediamine. The compound with resorcinol has also been brominated and the corresponding tetrabromo derivative prepared. The triple bond has been found to be unattacked during the process.

Condensation was not found to take place in the following cases: *o*-, and *p*-cresol, *o*-, *m*-, and *p*-xylenols and *m*-amidophenol. In the case of catechol and pyrogallol, although condensation had apparently occurred, yet the products could not be obtained in a state of sufficient purity for further examination or analysis.

Although condensations took place without the use of any condensing agent, yet the employment of a trace of concentrated sulphuric acid and in some cases, tin tetrachloride, was found to be beneficial in producing greater yield of the dyestuffs. Nevertheless it was found, however, that the yields obtained were very unsatisfactory on account of the formation of tarry by-products, and a considerable loss of the starting materials occurred during the condensation process. With the exception of the phenol compound, all the rest of the dyestuffs are strongly fluorescent in solution.

EXPERIMENTAL.

Phenol-acetylenein.—A mixture of acetylene dicarboxylic acid (2·1 g.), phenol (6 g.) and tin tetrachloride (15 g.) was heated in an oil-bath at 110-120° for 15 hours. The melt on cooling was poured into water and the excess of phenol distilled off in steam. The residue was extracted with concentrated ammonia, precipitated with hydrochloric acid and the process repeated a number of times. The brown product was finally purified by extraction with ether and crystallisation from the same solvent. It is a brownish yellow micro-crystalline substance, which shrinks at 115° and melts at 119-120° (decomp.). It is readily soluble in alcohol to a pink solution. In acetone, glacial acetic acid and ether a bright yellow solution is obtained. It is insoluble in water, chloroform, ligroin, benzene, petroleum ether and carbon disulphide. In dilute alkalis it dissolves with a brilliant pink colour and from the solution it is reprecipitated unchanged by acidification. (Found : C, 72·05 ; H, 3·82, $C_{16}H_{10}O_4$ requires C, 72·18; H, 3·76 per cent).

Resorcinol-acetylenein.—A mixture of acetylene dicarboxylic acid (1·5 g.), resorcinol (4 g.) and two drops of concentrated sulphuric acid was heated in an oil-bath at 120-130° for 8 hours. The reaction product was then dissolved in 5% cold caustic soda solution and after filtration it was reprecipitated with dilute hydrochloric acid. It was then dissolved in absolute alcohol and precipitated by dry ether. Finally it was crystallised from absolute alcohol in brown microscopic needles which decomposed at 185°. It dissolves in alcohol, acetone, acetic acid and pyridine forming bright yellow solutions with intense green flourescence. In dilute caustic alkalis it dissolves with an orange colour and the same bright green fluorescense. (Found : C, 67·67; H, 3·83. $C_{16}H_8O_5$ requires C, 67·77; H, 3·86 per cent).

Tetrabromoresorcinol-acetylenein.—The above compound (0·8 g.) dissolved in alcohol (40 c.c.) was treated with an excess of bromine in the same solvent and the mixture heated under reflux on the water-bath for 3 hours. On the addition of water a dark brown heavy liquid was precipitated which was separated by decantation and washed with mixed solutions of potassium iodide and sodium thiosulphate in order to remove the excess of bromine still present. On treatment of the heavy liquid with cold 2 % caustic soda, the greater portion of it dissolved forming a bright pink solution, while a small oily residue remained. The latter on examination was found to be bromoform and the pink solution on treatment with dilute hydrochloric acid precipitated the colouring matter in brick-red flocks which were collected and crystallised from glacial acetic acid in steel-blue needles with a golden metallic lustre. It melts at 115-117° (decomp.). (Found: Br, 53·46. $C_{16}H_6O_5Br_4$ requires Br, 53·51 per cent).

Phloroglucinol-acetylenein was obtained from phloroglucinol and acetylene dicarboxylic acid according to the method described above. The substance crystallises from absolute alcohol in brown microscopic needles which do not melt up to 310°. It dissolves in most of the organic solvents and also in dilute alkalis with a yellowish pink colour. (Found : C, 57·72; H, 3·77. $C_{16}H_8O_7, H_2O$ requires C, 58·09; H, 3·03 per cent).

Orcinol-acetylenein was obtained from orcinol and acetylene-dicarboxylic acid in a similar way to the above. It is a light yellow amorphous powder, m.p. 155-157° (decomp.) and dissolves in most of the organic solvents with a yellow colour and in dilute alkalis with a bright pink colour. The solution in each case has a dark green fluorescence. (Found : C, 69·96; H, 4·08. $C_{18}H_{12}O_5$ requires C, 70·13 H, 3·96 per cent).

m-*Dimethylamidophenol-acetylenein.*—A mixture of acetylene-dicarboxylic acid (2·5 g.), *m*-dimethylamidophenol (6 g.) and 4 drops of concentrated sulphuric acid was heated in an oil-bath at 130-140° for 8 hours. The cold melt was extracted with dilute hydrochloric acid and the filtered extract precipitated with dilute sodium carbonate. The pink coloured flocculent mass was filtered off and crystallised from 80% alcohol in fine pink needles, m.p. 126° (decomp.). It is easily soluble in alcohol and acetone, giving pink solutions with strong orange-brown fluorescence. In dilute acids also the same colour and fluorescence are observed. It is moderately soluble in chloroform, pyridine and ethyl acetate but dissolves only slightly in carbon disulphide and ether. It is completely insoluble in water, benzene and petroleum ether. (Found : N, 8·61. $C_{20}H_{18}O_3N_2$ requires N, 8·36 per cent).

m-*Diethylamidophenol-acetylenein* was prepared from acetylene-dicarboxylic acid and *m*-diethylamidophenol in a similar way to the above. It is a pink substance, having properties very similar to the above mentioned compound, m.p. 109° (decomp.). (Found : N, 7·39. $C_{24}H_{26}O_3N_2$ requires N, 7·18 per cent).

m-*Phenylenediamine-acetylenein.*—A mixture of acetylene-dicarboxylic acid (2 g.) and *m*-phenylenediamine hydrochloride (4·5 g.) was rapidly melted over a free flame and quickly cooled, the whole operation hardly taking more than 2 minutes. The dark red melt was extracted with absolute alcohol and filtered from the unchanged diamine hydrochloride. The addition of ether to the above filtrate precipitated the dyestuff in bright yellow flocks which were collected and crystallised from 90% alcohol in light brown microscopic needles which decompose without melting at 260°. The constitution of the compound has been assumed to possess an acridine ring structure in accordance with the work of the previous workers in this line (*cf.* Ghosh, *J. Chem. Soc.*, 1919, **115**, 1102; Sircar and Dutt, *ibid.*, 1922, **121**, 1285; Dutt, *ibid.*, 1922, **121**, 2389; 1923, **123**, 225; Tewari and Dutt, *J. Indian Chem. Soc.*, 1926, **2**, 161; 1927, **3**, 201; 1928, **4**, 59).

The substance is fairly soluble in alcohol, acetone, acetic acid and pyridine, slightly soluble in ethyl acetate, chloroform and water and completely insoluble in ether, benzene, carbon disulphide, ligroin and petroleum ether. (Found: N, 15·54. $C_{16}H_{11}O_2N_3$ requires N, 15·17 per cent).

Absorption maxima of the acetyleneins and their analogues.

Compound.	Acetylenein.	Malein.	Citraconein.	Itaconein.
Phenol-	5210	...	...	...
Resorcinol-	5180	4890	4940	4880
Tetrabromo resorcinol-	5600	5180	5490	...
m-Diethylamido-phenol-	5670	5400	5560	5470
Phloroglucinol-	5640	...	...	...

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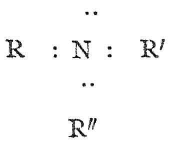
The Stereochemistry of Trivalent Nitrogen Compounds. Part I. The Attemped Resolution of Some Substituted Derivatives of Aniline.

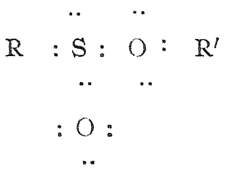
By E. V. Menon and D. H. Peacock.

Mills and Elliott (*J. Chem. Soc.*, 1928, 1298) resolved benzenesulphonyl 8-nitro-1-naphthylglycine but ascribed the dissymmetry to the restriction of the free rotation of the nitrogen atom and not to the absence of a planar configuration for this atom. With the exception of this compound and some others of a similar type (Mills and Breckenridge, *Trans. Faraday Soc.*, 1930, 431) no substance appears to be known in which the optical activity arises from a nitrogen atom not doubly linked to carbon or forming part of a ring. In view of the close formal resemblance between the electronic configurations of trivalent nitrogen compounds of type I and the sulphinic esters (II)



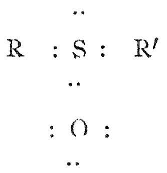
$\mathrm{R} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}} : \mathrm{R'}$, with $\mathrm{R''}$ below N

(I)



$\mathrm{R} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} : \mathrm{R'}$, with $: \underset{\cdot\cdot}{\mathrm{O}} :$ below S

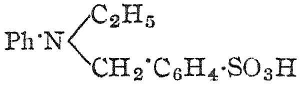
(II)



$\mathrm{R} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}} : \mathrm{R'}$, with $: \underset{\cdot\cdot}{\mathrm{O}} :$ below S

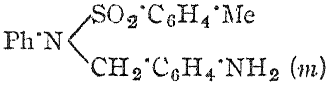
(III)

and sulphoxides (III) it appeared desirable to attempt the resolution of the following compounds :—



$\mathrm{Ph{\cdot}N}\left\langle\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{CH_2{\cdot}C_6H_4{\cdot}SO_3H}\end{matrix}\right.$

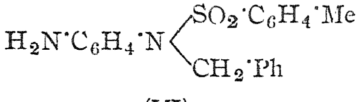
(IV)



$\mathrm{Ph{\cdot}N}\left\langle\begin{matrix}\mathrm{SO_2{\cdot}C_6H_4{\cdot}Me}\\ \mathrm{CH_2{\cdot}C_6H_4{\cdot}NH_2}\ (m)\end{matrix}\right.$

(V)

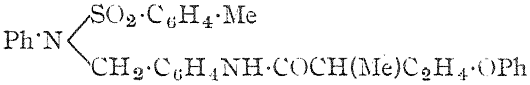
(*m* or *p*)



$\mathrm{H_2N{\cdot}C_6H_4{\cdot}N}\left\langle\begin{matrix}\mathrm{SO_2{\cdot}C_6H_4{\cdot}Me}\\ \mathrm{CH_2{\cdot}Ph}\end{matrix}\right.$

(VI)

The compound (IV) readily gave a crystalline brucine salt from which, after repeated crystallisations, only an inactive sodium salt was obtained; no other crystalline salt could be obtained with the alkaloids tried (*cf.* Peacock, *Dissertation*, London University, 1927; Meisenheimer, *Ber.*, 1924, **56**, 1744; Jones and Millington, *Proc. Camb. Phil. Soc.*, 1904, **12**, *vi*, 489). The compounds (V) and (VI) readily gave crystalline tartrates but these salts could not be resolved. The compound (VI, *m*) was converted into the methiodide in the hope that the strongly basic quaternary salt would readily give a crystalline camphorsulphonate or bromcamphorsulphonate but both these salts failed to crystallise. The compound (V) was condensed with α-methyl-γ-phenoxybutyryl chloride and gave (VII)



$$\mathrm{Ph{\cdot}N}\left\langle\begin{array}{l}\mathrm{SO_2{\cdot}C_6H_4{\cdot}Me}\\ \mathrm{CH_2{\cdot}C_6H_4NH{\cdot}COCH(Me)C_2H_4{\cdot}OPh}\end{array}\right.$$

(VII)

but this substance appeared homogeneous (*cf.* Kipping and Salway, *J. Chem. Soc.*, 1904, 438). The compound VI (*meta* and *para*) behaved similarly. None of the substances examined showed signs of dissymmetry.

In the course of this work it was observed that the sodium salt of *p*-toluenesulphonyl-*p*-nitroaniline reacted with benzyl chloride much less readily than did the corresponding derivatives of *m*-nitraniline. This behaviour resembles that of *m*- and *p*- nitranilines with benzyl chloride (Peacock, *J. Chem. Soc.*, 1925, **127**, 2177) and is being further examined.

EXPERIMENTAL.

Brucine salt of ethylbenzylaniline sulphonic acid (IV).—Ethylbenzylaniline was sulphonated with 20% oleum at 80°. The crystalline acid and brucine in molecular proportions were dissolved in hot alcohol and the solution allowed to cool, when the brucine salt separated in long needles, m. p. 164-5°, sparingly soluble in cold alcohol and less soluble in the other common organic solvents. (Found: S, 4·75, 4·48, 4·65. $C_{38}H_{43}O_7N_3S$ requires, S, 4·67 per cent). This compound was crystallised 5 times from alcohol and then converted to the sodium salt which was found inactive.

p-Toluenesulphonylbenzyl- m *-nitroaniline.*—*p*- Toluenesulphonyl-*m*-nitroaniline was prepared by a slight modification of the method described by Morgan and Micklethwait (*J. Chem. Soc.*, 1906, **89**, 1292). *m*-Nitraniline (69 g), *p*-toluenesulphonyl chloride (47·6 g.) and toluene (500 c. c.) were heated on a water-bath under reflux condenser until the evolution of hydrogen chloride ceased (20 hours). Toluene (100 c. c.) was then added and the *m*-nitraniline extracted by concentrated hydrochloric acid. The sulphonyl derivative was then extracted by caustic soda, acidified with hydrochloric acid and crystallised from alcohol, m. p. 136-7°, yield 87%. This substance (58·4 g. with caustic soda (8 g.) was dissolved in warm alcohol (300 c.c.) and) benzyl chloride (25·3 g.) added. The mixture was boiled under reflux on a water-bath until neutral (4 hours). The solvent was distilled off, the residue extracted with dilute caustic soda and the pale yellow product (58 g.) crystallised from alcohol, m. p. 118°. (Found : N, 7·4 ; S, 8·42. $C_{20}H_{18}O_4N_2S$ requires N, 7·33 ; S, 8·37 per cent).

*p-Toluenesulphonyl-benzyl-*m*-phenylenediamine* (VI, meta)—The nitro compound (50 g.) was dissolved in alcohol (250 c. c.) and tin (50 g.) added. Hydrochloric acid (85 c.c.) was added, 5 c.c. at a time, and the mixture heated under reflux for 6 hours on a water-bath. The solvent was removed by distillation and the residue basified with sodium carbonate. The mixture of tin oxide and base was filtered and the base extracted with hot alcohol, when the base was obtained as colourless crystals, rapidly darkening on exposure to air, m. p. 127°, yield 40 g. (Found ; N, 7·9 ; S, 8·86. $C_{20}H_{20}O_2N_2S$ requires N, 7·96; S, 9·09 per cent). The *acid tartrate* crystallised on cooling by adding tartaric acid (6·0 g.) to the base (14 g.) dissolved in warm alcohol (100 c. c.), m. p. 136°. It is very soluble in acetone and chloroform, sparingly soluble in cold alcohol and benzene. (Found : N, 5·77; S, 6·48. $C_{24}H_{26}O_8N_2S$ requires N, 5·57; S, 6·37 per cent). The salt was crystallised from alcohol, $[\alpha]_D^{28}$ (acetone, p=5·024 g.), 4·57°; whence $[M]_D^{28}=23·0°$. After three crystallisations the solution (p= 5·0196 g.) had $[\alpha]_D^{28}$, 4·67°; $[M]_D^{28}$, 23·5, and after twelve crystallisations $[\alpha]_D^{28}$, 4·57 ; $[M]_D^{28}$, 23·1° (p=5·0224 g.). The salt isolated from the mother liquors had $[\alpha]_D^{28}$, 4·57°; $[M]_D^{28}$, 23·1° (p=5·0204 g.). *p*-Toluidine hydrogen tartrate in acetone (p=2·5672 g.) had $[\alpha]_D^{28}$, 8·56° ; $[M]_D^{28}$, 22·0°. No resolution seems, therefore, to have been effected.

p - *Toluenenesulphonyl*-m - *dimethylaminophenylbenzylamine.*—The amine (7 g.) was mixed with water (100 c. c.), sodium carbonate (3·2 g.) and methyl iodide (6 g.) and heated under reflux on a water-bath for 3 hours. Caustic soda was added and the oily base solidified on cooling and finally crystallised from alcohol, m. p. 101°, yield 7 g. (Found : N, 7·53. $C_{22}H_{24}O_2N_2S$ requires N, 7·37 per cent).

The *methiodide* of the preceding compound was prepared in two ways: *(a)* The tertiary base (3·5 g.) was mixed with methyl iodide (2·0 g.) and left for some days. The excess of methyl iodide was removed by evaporation and the residue crystallised from alcohol, m.p. 111°. *(b)* The primary base (VI) (3·5 g.), methyl iodide (5 g.) and water (100 c. c.) were heated under reflux on a water-bath for 5 hours. The quaternary salt separated as an oil which solidified when cold and was finaly crystallised from alcohol, m.p. 111-112°. (Found : I, 23·95. $C_{23}H_{27}O_2N_2IS$ requires I, 24·32 per cent). This iodide with silver bromcamphor sulphonate gave only a gummy product.

α-Methyl-γ-phenoxybutyryl derivative of (VI) (meta).—The amine (VI, meta) (3·5 g) was dissolved in ether and α-methyl-γ-phenoxybutyryl chloride (2·3 g.) in ether (25 c. c.) added. The reaction was vigorous. The ether was distilled off and the amine hydrochloride removed by dilute hydrochloric acid. The amide was left as an oil which solidified after some days. It was crystallised 5 times from alcohol, each fraction melting at 117° ; from the mother liquors the recovered substance melted at 116°, mixed m. p. 115-16°. (Found : N, 5·44. $C_{31}H_{32}O_4N_2S$ requires N, 5·29 per cent). The product seems homogeneous. α-methyl-γ-phenoxybutyric acid was prepared by the methylation of β-phenoxyethyl malonic ester prepared by the action of β-phenoxyethyl-*p*-toluenesulphonate on sodiomalonic ester (Peacock and Tha, *J. Chem Soc.*, 1928, 2303). The acid was converted into the acid chloride by thionyl chloride.

p-*Toluenesulphonylbenzyl*-p-*nitroaniline*.—*p*-Toluenesulphonyl-*p*-nitraniline (58·4 g., Morgan and Micklethwait, *loc. cit.*) was mixed with caustic soda (8·0 g.) in amyl alcohol (350 c. c.) and benzyl chloride (25·3 g.) added. The mixture was boiled for 12 hours under reflux in an oil-bath at 140-50° until neutral. In ethyl alcohol it was not neutral after a much longer period of heating. The amyl alcohol was distilled off from on oil-bath and the residue extracted with caustic soda solution. The product (54 g.) separated from alcohol in pale-yellow crystals, m.p. 128°. (Found : N, 7·5 ; S, 8·18. $C_{20}H_{18}O_4N_2S$ requires N, 7·33 ; S, 8·37 per cent).

p-*Toluenesulphonyl-benzyl*-p-*phenylenediamine* (VI, para).—The nitro compound from the above (38·2 g.) was dissolved in alcohol (200 c. c.) and tin (40 g.) added. Concentrated hydrochloric acid (90 c. c.) was then added, 10 c. c. at a time, and reduction completed by heating on a water-bath for 8 hours. The product was worked up as before, yield of crude base 28 g. It separated from alcohol in colourless crystals rapidly turning brown, m.p. 162°. (Found ; N, 8·02 ; S, 8·87. $C_{20}H_{20}O_2N_2S$ requires N, 7·96 ; S, 9·09 per cent). This base did not form a tartrate and the camphorsulphonate and bromcamphorsulphonate were non-crystalline.

α-methyl-γ-phenoxybutyryl derivative of (VI, para).—This was prepared from the base and the acid chloride in ether solution. The amide was crystallised 7 times from alcohol, m. p. of each fraction being 143°. The amide, recovered from the mother liquor, melted at 142°, mixed m. p. 142-3°. (Found : N, 5·22. $C_{31}H_{32}O_4N_2S$ requires N, 5·29 per cent).

p-*Toluenesulphonyl*-[m-*nitrobenzyl*]-*aniline*.—Sodium (2˙3 g.) was disolved in alcohol (100 c. c.) and *p*-toluenesulphoanilide (24˙7 g.) added. The mixture was boiled under reflux on a water-bath for 10 minutes and the alcohol then distilled off. *m*-Nitrobenzyl chloride (17˙2 g.) was added to the sodium compound, dried by two distillations with dry benzene, and the mixture heated in an oil-bath at 140-50° for 15 hours. The product was extracted with caustic soda solution and crystallised from alcohol, m. p. 95°. (Found : N, 7·28 ; S, 8·28. $C_{20}H_{18}O_4N_2$ S requires N, 7·33 ; S, 8·37 per cent).

p-*Toluenesulphon*-[m-*aminobenzyl*]-*anilide* (V).—The nitro compound from the above (30 g.) was dissolved in alcohol (200 c. c.) and tin (30 g.) added. Concentrated hydrochloric acid (55 c c.) was then added gradually and reduction completed by heating for 5 hours under reflux on a water-bath. The product was worked up as before. The base (24 g.) was crystallised from alcohol, m. p. 129°. (Found : N, 7˙98 ; S, 8˙81. $C_{20}H_{20}O_2N_2S$ requires N, 7˙96 ; S, 9˙09 per cent). The base V (14˙0 g.) was dissolved in alcohol and tartaric acid (6˙0 g.) added. The acid tartrate separated on cooling, m. p. 133°. (Found : N, 5˙68 ; S, 6˙21. $C_{24}H_{26}O_8N_2S$ requires N, 5˙57 ; S, 6˙37 per cent). After one crystallisation $[\alpha]_D^{28}$ in acetone (p= 4·9992 g.), 4·6° ; $[M]_D^{28}$, 23·0°, and after five crystallisations, $[\alpha]_D^{28}$, 4·6° ; $[M]_D^{28}$, 23·0° (p=5·0192 g.). No resolution appears to have been effected. The camphor sulphonate and the bromocamphorsulphonate were not obtained crystalline.

α-methyl-γ-phenoxybutyryl derivative of (V) was prepared in the usual way in ether solution. It was fractionally crystallised from alcohol 5 times and each fraction melted at 111°. The product recovered from the mother liquors melted at 110° ; mixed m. p. 109-10°. (Found : N, 5˙48. $C_{31}H_{32}O_4N_2S$ requires N, 5.29 per cent).

We have to thank the University of Rangoon for a grant in aid of this work which is being continued.

Received June 15, 1935.

Constituents of the Seeds of *Blepharis Edulis*, Pers. Part I.

BY JAGRAJ BEHARI LAL.

Blepharis Edulis, Pers., belongs to the natural order of *Acanthaceae*, and under the local name of *utanjan* and the Persian name *Anjurah*, is sold in the Indian Bazars as a standard Indian medicine. "Medicinally, the seeds are considered to be attenuate, resolvent, diuretic, aphrodisiac, expectorant and deobstruent" (Dymock, *Pharmacographica Indica*, III, 41-42).

The bitter principle of the seeds is described (Dymoc, *loc.cit.*) as a white crystalline body, soluble in water, amyl and ethyl alchol but insoluble in ether and petroleum ether and as giving a red colour with concentrated sulphuric acid, a violet colouration with ferric salts and an agreeable odour of salicylaldehyde on treatment with sulphuric acid and potassium dichromate. The presence of a white crystalline non-bitter principle melting at 225° and giving no colour reactions with concentrated sulphuric acid and ferric salts has also been noticed.

As the result of the present investigation a bitter glucoside *Blepharin* (yield 1·2%), melting at 222° with previous shrinking at 220° and having the formula $C_{16}H_{20}O_{11}$, and a tasteless nitrogenous compound having the formula $C_4H_6O_3N_4$, melting with decomposition at 225-226° with previous darkening in colour at 218° and identified as *dl*-allantoin (yield 2.1%), have been isolated. The isolation of allantoin in more than 2% yield from the seeds of *Blepharis Edulis* is not surprising since it is known to occur frequently in the plant kingdom.*

EXPERIMENTAL.

The seeds of *Blepharis Edulis*, about a year old, were ground to a coarse powder in a grinding machine. When completely burnt it left 7·23% of a greyish white ash, in which the following elements and radicals were detected: sodium, potassium, calcium, magnesium, iron, silica, alumina, carbonate, phosphate, chloride, nitrate, and sulphate (in traces). In order to ascertain the general character of the constituents, 50 g. of the powdered seeds were extracted successively in a Soxhlet's apparatus with various solvents in the order given below whereby the following amounts of extracts, dried at 100° to constant weight, were obtained.

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* *cf.* Schulze and Barbieri, *J. pr. Chem.*, 1882, *ii*, **25**, 145; Fosse, Thomas and Graeve, *Compt. rend.*, 1934, **198**, 1953; *J. Chem. Soc.*, Abstracts, 1897, *ii*, 118; Plants, *Chem. Zentral.*, 1910, *i*, 1622; Schulze and Booshard, *Z. physiol. Chem.*, **9**, 420; *J Chem. Soc.*, Abstracts, 1919, *i*, 60.

1. *Benzene Extract* (3·72%):— A dark reddish brown thick oil smelling strongly of the seeds was obtained.

2. *Chloroform Extract* (1·02%).—It was a syrupy brown tasteless extract containing suspended globules of white fatty matter. Its alcoholic solution gave a greenish black colour with ferric chloride showing the presence of tannins and became milky on dilution with water.

3. *Ethyl Acetate Extract* (17·25%).—It was a brown extract of extremely bitter taste and consisted of a white crystalline mass along with large amount of tannin matter, as it gave black colouration and then a black precipitate with ferric chloride, and a flocculent yellow precipitate with lead acetate solution and reduced Fehling's solution copiously. It gave no colour reactions with alkaloidal reagents.

4. *Alcoholic Extract* (6·04%.)—It was of a syrupy nature and slightly bitter in taste and contained a tasteless white crystalline mass. It reduced Fehling's solution copiously and gave a black colouration with ferric chloride.

5. *Test for Enzymes.*—A quantity (50 g.) of the ground seeds was macerated with distilled water at ordinary room temperature (22°) for 2 days with the addition of a little toluene to prevent bacterial action. The mucilageous mass was filtered and the filtrate tested as usual for enzymes. Peroxidase, catalase, and invertase were totally absent but diastase was present in minute quantity.

A preliminary examination for the presence of alkaloids was made with 200 g. of the powdered drug which was repeatedly extracted with Prollius fluid. The filtrate after concentration was extracted with dilute hydrochloric acid and the acid extract was treated with alkaloidal reagents with negative results.

For complete analysis 9·0 kg. of the powdered seeds were in lots of 0·7 kg. exhaustively extracted with benzene in a 5 litre extraction flask, the extract concentrated and 342 g. of a thick reddish brown, fragrant, semi-drying oil were obtained. The oil-free powdered drug was extracted with rectified spirit, till a portion of the extract did not leave any appreciable amount of crystalline matter on complete evaporation of the solvent. The combined extract, on concentration on the water-bath to one seventh of its volume and on allowing to stand at ordinary temperature for about a week, deposited a large amount of crystalline matter, which was filtered at the pump. The residue was washed with alcohol until it had assumed a white or at most a light brownish colour. Thus 230 g. of a tasteless and greasy crystalline stuff were obtained, which after repeated extraction with hot benzene in order to remove oily and fatty matter became brown at 210°, softened at 215° and melted at 218° (decomp.). It is tasteless and almost insoluble in all the organic solvents. It was twice crystallised from boiling water as glistening monoclinic prisms, m.p. 225-26° with previous darkening in colour at 218°. The air-dried substance has the composition $C_4H_6O_3N_4$ and contains no water of crystallisation.

Its solution is not coagulated by tannic acid and does not respond to the ninhydrin reaction of amino acids. It does not reduce Tollen's reagent and Fehling's solution. It does not give any colouration with neutral ferric chloride, nor any precipitate with lead acetate, basic lead acetate, calcium chloride or cadmium chloride. It dissolves in moderately strong mineral acids in the cold to a colourless solution and in dilute ammonia and alkali hydroxides. On heating with concentrated nitric acid no yellow or brown colouration appears. It readily reduces alkaline permanganate even in the cold but acid potassium permanganate only on heating. It evolves ammonia with alkali hydroxides. It does not give positive results in carbylamine, Bulow's, Biuret, and Mureoxide tests. With nitrous acid it evolves nitrogen. It gives with mercuric nitrate a white precipitate which is soluble in boiling water. [Found: C, 30·83, 30·51, 30·47; H, 4·08, 3·98, 3·79; N, 35·9, 35·6; M. W. (ebulioscopically in water), 131, 135. $C_4H_6O_3N_4$ requires C, 30·42; H, 3·8; N, 35·4 per cent. M. W. 150).

Action of Concentrated Nitric acid.—30 C.c. of concentrated HNO_3 (*d* 1·4) was gradually poured on to the powdered substance (3 g.) when it first puffed up and then crumbled to powder. The excess of acid was evaporated on the water bath-when a slightly sticky granular stuff was left behind, which crystallised from a small quantity of boiling alcohol in fine tiny needles. The air-dried crystals fused at 200° to an opaque mass, evolved gas at 200-210° and turned deep brown and decomposed at 225° and were identified as those of allanic acid. (Found in sample dried at 125°: C, 23·29; H, 2·51; N, 34·72. $C_4H_5O_5N_5$ requires C, 23·65; H, 2·46; N, 34·48 per cent). The silver salt, prepared by the usual method, darkened at 195° and decomposed at 199°. (Found: Ag, 34·94. $C_4H_4O_5N_5Ag$ requires Ag, 34·83 per cent). The solution of the substance (2 g.) in the smallest amount of ammonium hydroxide was allowed to stand in open air for several days. On complete evaporation of water ammonium allantoate was obtained as a crystalline powder. (Found : C, 24·72 ; H, 5·80 ; N, 36·9. $C_4 H_{11}O_4N_5$ requires C, 24·86; H, 5·70 ; N, 36·37 per cent). By the action of aqueous caustic potash or soda and subsequent precipitation with absolute alcohol potassium or sodium allantoate were obtained. (Found: C, 22·21 ; H, 2·78. $C_4H_7O_4N_4K$ requires C, 22·42; H, 2·60 per cent). (Found in a sample dried over calcium chloride : C, 22·01; H, 4·34. $C_4H_7O_4N_4Na$, H_2O requires C, 22·22 ; H, 4·16 per cent).

Preparation of Allantoin.—20 G. of uric acid were suspended in 400 c.c. of water and dissolved by the careful addition of caustic soda in small quantity at a time and with constant stirring. The alkaline solution was treated with a 5% solution of 13 g. of potassium permanganate and well stirred. As soon as the solution was decolourised it was filtered from manganese dioxide and the filtrate acidified with acetic acid and evaporated (best in vacuo) until crystals appear. After three crystallisations from hot water it melts at 225° (decomp.) after pervious darkening in colour at 218° and this remained undepressed by admixture with the non-bitter principle. (m.p. of allantoin 229° recorded in literature).

Isolation of Blepharin.—The filtrate and washings after the separation of allantoin were concentrated and allowed to stand for a few days, but crystals did not appear. It was then repeatedly extracted with hot ethyl acetate, after a few extractions with hot benzene till the syrupy mass was no longer bitter. The ethyl acetate layer was decanted from the heavy viscous syrupy mass and was concentrated to one seventh of its volume and on allowing to stand for a week became semi-solid due to the separation of glistening tiny needles which were filtered off at the pump after thinning with a mixture of ethyl alcohol and ethyl acetate (1 : 4). Some more of the crystalline stuff was obtained from the filtrate and washings after concentration and allowing to stand for a number of days. After removal of oily and fatty matter by extraction with hot benzene, it was repeatedly crystallised from hot alcohol till the air dried material mleted at 219-20° with previous shrinking at 213°. After two crystallisations from acetone it was obtained as glistening stout needles and the air-dried material melted at 220° after shrinking at 220°. It is proposed to name this bitter principle as *Blepharin*.

It is sparingly soluble in cold water and more soluble in boiling water. It is slightly soluble in cold acetone, amyl alcohol, ethyl acetate, methyl alcohol and fairly in the hot. It is insoluble in ether, petroleum ether, benzene, chloroform, bromoform and carbon tetrachloride. Caustic alkali and alkali carbonate solutions have no action on it. It gives no precipitate in aqueous or alcoholic solution with silver nitrate, calcium chloride, ferric chloride, lead acetate, or copper acetate. With concentrated sulphuric acid it gives no colouration in the cold but a purple red colonration appears immediately on warming. With concentrated sulphuric acid containing 1% potassium dichromate it gives a fine violet colouration in the cold ; while with concentrated sulphuric acid containing sufficient potassium dichromate it gets carbonised and gives the odour of burnt sugar. With ferric chloride in aqueous or alcoholic solution it gives no colouration and reduces Tollen's reagent and Fehling's solution only after hydrolysis with dilute mineral acids. With alcoholic caustic potash it does not give any colouration in the cold or on heating.

To a quantity of the substance (0·01 g.) in water (1 c.c.) 2 drops of a solution of α-naphthol (10% in chloroform) and 1 c.c. of concentrated H_2SO_4 were added when a reddish violet ring and on shaking a bluish violet precipitate was formed (Molisch's test). A small quantity of blepharin, dissolved in acetic anhydride, gave on addition of a drop of concentrated sulphuric acid a pinkish violet colouration which deepened on standing (Libermann's cholesterol reaction). To its solution in glacial acetic acid, 1 c.c. of chloroform and a few drops of concentrated sulphuric acid were added when a permanent pink colour appeared (Hager-Salkowski reaction). It gave a negative Keller-Killiani reaction. [Found (in sample dried at 120-125°) : C, 48·94, 49·03 ; H, 5·39, 5·41 ; M.W. in phenol (cryoscopic) 306, 330 ; $C_{16}H_{20}O_{11}$ requires C, 49·5 ; H, 5·16 per cent. and M. W. 388].

The ethyl acetate mother liquor which did not deposit any more crystal and still had an intensely bitter taste was evaporated to remove ethyl acetate and the residue dissolved in water with constant stirring and the solution treated with a solution of lead acetate. The resulting greyish yellow precipitate was filtered off, well washed first with hot water and then with alcohol and after decomposition with hydrogen sulphide in alcoholic suspension gave a reddish brown solution. After removal of sulphuretted hydrogen by a current of carbon dioxide and on concentration under reduced pressure it deposited no crystalline mass. It was extracted with benzene which removed a trace of fatty matter and extractions with chloroform, ethyl acetate, acetone did not result in the isolation of any crystalline matter. The alcoholic solution on complete removal of the solvent left a dark brown sticky mass which consisted mostly of catechol, tannins and saponins, since on shaking it with water a large amount of foam resulted. It gave an intense blue colouration on addition of potassium ferricyanide containing a little ferric chloride, and a black colouration and then a precipitate with ferric chloride, a red colouration with concentrated sulphuric acid, reduced Tollen's reagents on warming, and mercuric chloride on long heating precipitated gelatine from solution and gave a greenish white precipitate with tartar emetic and a deep red colouration with potassium ferricyanide and ammonia.

The aqueous filtrate and washings from the afore mentioned lead acetate precipitate gave a yellow precipitate on treatment with excess of basic lead acetate. This on being worked up as before gave a brown alcoholic solution from which on concentration no precipitate separated.

The aqueous filtrate from the above basic lead precipitate was treated with hydrogen sulphide and the light yellow filtrate after separation of lead sulphide was concentrated on the water bath to a small volume and was found to contain besides a large excess of glucose and acetic acid a small amount of a crystalline substance which has not yet been obtained in sufficient quantity. The mother liquor reduced Fehling's solution copiously and on treatment with phenylhydrazine an osazone was formed which was found to be identical with phenylglucosazone, m.p. 206°.

The author wishes to convey his heartiest thanks to Dr. S. Dutt, D.Sc., P.R.S., for his keen interest in the work and to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship, which enabled him to undertake this investigation.

Further work on the elucidation of the constitution of blepharin is in progress.

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Active Principle of *Myrsine Africana*, Linn.

BY S. KRISHNA AND B. S. VARMA.

During a search for indigenous drugs, reputed to be of value as anthelmintics, the chemistry of the active constituents of *Myrsine africana* was studied. It is a small, evergreen, pubescent shrub known as *bebrang* in Hindi, belonging to the same family as *Embelia ribes* (N. O. *Myrsinacea)* but botanically quite distinct. In local bazaars, no such distinction is made between the berries of the two species and both of them are called by the same name, although *M. africana* is less commonly known and its berries are much smaller in size than that of *E. ribes*. The berries are used in Ayurvedic system of medicine as anthelmintic, especially in cases of tape worm and are also used in preparation of ointments for ringworm and other skin diseases. For our investigation authentic berries were collected through the forest officers of the Chakrata division (U. P.)

The dried berries on extraction with various organic solvents gave a crystalline material of golden colour which was identified as embelic acid through preparation and identification of its many derivatives (Kaul, Ray and Dutt, *J. Chem. Soc.*, 1929, 577; Hasan and Stedmann, *ibid.*, 1931, 2112). The berries when extracted with rectified spirit deposited along with the colouring matter, a white crystalline material which has been identified as quercitol. The presence of quercitol in *E. ribes* has not been reported by previous workers.

EXPERIMENTAL.

The dried and finely powdered berries were soaked in petroleum ether for 48 hours to remove the fatty ingredients, after which it was filtered under pressure and spread out in the sun to dry. This on extraction, in a Soxhlet, with chloroform deposited golden coloured crystalline plates (yield 3 %). These were removed and crystallised from rectified spirit in golden yellow plates, m.p. 143-44°. It gave a diacetyl derivative (m. p. 54°), a dibenzoyl derivative (m. p. 95-96°), dianilino derivative (m. p. 160-62°) and dioxime (m.p. 276°), which have been found identical with the corresponding derivatives obtained from embelic acid.

The residue left over after extraction of embelic acid, was further extracted with rectified spirit. The alcoholic extract on concentration and standing deposited a brown mass of crystals which on separation were boiled with chloroform. This treatment removed the colouring matter and left a white crystalline residue which on crystallisation from water and purification gave colourless prisms, m. p. 228-30° (yield 1%). (Found: C, 44·0; H, 7·7 per cent).

This crystalline substance is practically insoluble in most of the organic solvents but dissolves readily in hot water. It has a slightly sweetish taste and is neutral in reaction; does not form precipitate with lead acetate and has an optical rotation of $[\alpha]_D = +24°$ in water. On oxidation with manganese dioxide in acid solution it gives off acrid smell reminding of benzoquinone. It gives an amorphous pentaacetyl derivative. These properties and reactions establish the crystalline product to be quercitol.*

The berries of *E. ribes* were also examined and quercitol was isolated and identified. The presence of *d*-quercitol in *Myrsine africana* and *E. ribes* is nothing surprising since it has been found in several other plants namely in *Fragaceae, Menispermaceae, Myrtaceae, Sapotaceae, Loganiaceae* and others.

*There was not enough material to isolate and identify the products of permanganate oxidation (Kiliani and Schafer, *Ber.*, 1896, **29**, 1762). Attempt was not made to collect more material to do this because analysis, m.p., rotation and other properties all tended to show that it was *d*-quercitol. Muller (*J. Chem. Soc.*, 1907, **91**, 1766) has established the identity of quercitol, isolated from the leaves of *Chamacrops humilis* on similar evidence.

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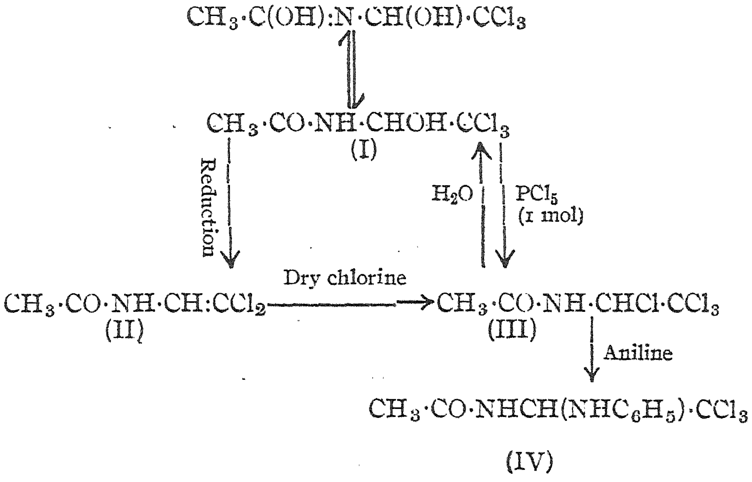
Constitution of the Reduction Product of Chloral Acetamide

BY (LATE) A. N. MELDRUM AND G. M. VAD.

Meldrum and Bhojraj (*Proc. Indian Science Congress*, 1926, 146) studied the reduction of chloral acid amides having the general formula $R{\cdot}CO{\cdot}NH{\cdot}CHOH{\cdot}CCl_3$. Yelburgi and Wheeler (*J. Indian Chem. Soc.*, 1934, **11**, 217)* brought forward evidence to show that the reduction products of these chloral amides had the general formula $R{\cdot}CO{\cdot}NH{\cdot}CH{:}CCl_2$. The experiments now described confirm Yelburgi and Wheeler's formula. Dichloroethyleneacetamide (II), which is obtained by the reduction of chloral acetamide (I) (Meldrum and Bhojraj, *loc. cit.*), reacts with dry chlorine to give β-trichloro-α-chloroethylacetamide (III) which is also obtained by the action of PCl_5 (1 mol.) on (I). (III) with water gives (I), and with aniline gives (IV).



$$\begin{tikzcd}
& \mathrm{CH_3{\cdot}C(OH){:}N{\cdot}CH(OH){\cdot}CCl_3} \arrow[d, shift left] & \\
& \underset{(I)}{\mathrm{CH_3{\cdot}CO{\cdot}NH{\cdot}CHOH{\cdot}CCl_3}} \arrow[u, shift left] \arrow[dl, "\text{Reduction}"'] \arrow[dr, shift left, "PCl_5\ (1\ \text{mol})"] & \\
\underset{(II)}{\mathrm{CH_3{\cdot}CO{\cdot}NH{\cdot}CH{:}CCl_2}} \arrow[rr, "\text{Dry chlorine}"] & & \underset{(III)}{\mathrm{CH_3{\cdot}CO{\cdot}NH{\cdot}CHCl{\cdot}CCl_3}} \arrow[ul, shift left, "H_2O"] \arrow[d, "\text{Aniline}"] \\
& & \underset{(IV)}{\mathrm{CH_3{\cdot}CO{\cdot}NHCH(NHC_6H_5){\cdot}CCl_3}}
\end{tikzcd}$$

EXPERIMENTAL.

β-Trichloro-α-chloroethylacetamide (III).—Dry chlorine was passed below 60° through a chloroform solution of (II) for 1 hour. Any chloral acetamide, which separated on keeping for two hours, was removed

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[*] (III) and (IV) of Yelburgi and Wheeler's paper (*loc. cit.*, p. 218) should be

$$\underset{\substack{\text{(unstable)}\\ \text{(III)}}}{\mathrm{R{\cdot}CO{\cdot}NH{\cdot}CHCl{\cdot}CHCl_2}} \xrightarrow{H_2O} \underset{\text{(IV)}}{\mathrm{R{\cdot}CO{\cdot}NH{\cdot}CHOH{\cdot}CHCl_2}}$$

and the filtrate was evaporated to yield (III) which was crystallised from dry benzene, m.p. 128°. (III) was also obtained from PCl_5 (1 mol) and (I), the reaction product being treated with petroleum ether to remove $POCl_3$. (Found : Cl, 62·6. $C_4H_5ONCl_4$ requires Cl, 63·0 per cent).

β-Trichloro-α-anilinoethylacetamide (IV), which was obtained by spontaneous interaction of (III) (3 g.) and aniline (1·5 g.) in benzene, was washed with dilute hydrochloric acid and crystallised from chloroform, m.p. 146°. (Found : Cl, 37·4. $C_{10}H_{11}ON_2Cl_3$ requires Cl, 37·8 per cent).

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Condensation of Chloral and Bromal with Polyhydric Alcohols.

BY (LATE) A. N. MELDRUM AND G. M. VAD.

This paper describes the preparations and reactions of the condensation products of chloral and bromal with ethylene glycol and glycerol, and of chloral with erythritol. Bromal is found to be more reactive than chloral.

The results are shown diagramatically in Figs. 1 and 2.

EXPERIMENTAL.

s-*Di-(β-trichloro-α-hydroxy-ethoxy)ethane* (I) was prepared by the method of Forcrand (*Bull. Soc. chim.*, 1889, *iii*, **2**, 256).

Anhydrodichloral-glycol (II) was obtained by keeping a solution of (I) in acetic anhydride and a few drops of concentrated sulphuric acid for 4 hours and diluting with water or by refluxing a mixture of (I) and acetyl chloride in equal proportions for 30 minutes and pouring into water. (II) separates from alcohol in cubes, m.p. 144°. (Found: Cl, 62·8. $C_6H_6O_3Cl_6$ requires Cl, 62·8 per cent).

It is stable towards hot concentrated nitric acid, boiling alkali solutions and strong ammonia in a sealed tube at 110°. Hot concentrated sulphuric acid changes it back into the original substances.

The diacetyl derivative of (I) (III) was obtained by keeping a solution of (I) (12 g.) and acetic anhydride (15 c.c.) for 4 hours and fractionating the product, b. p. 132-134°/15 mm. (Found: Cl, 48·5. $C_{10}H_{12}O_6Cl_6$ requires Cl, 48·2 per cent).

β-Trichloroethylideneglycol (IV) was formed by the distillation of (I) at atmospheric pressure, m. p. 42°; b. p. 200°. (Found: Cl, 55·6. $C_4H_5O_2Cl_3$ requires Cl, 55·5 per cent).

ββ-Dichloroethylideneglycol (V) was obtained by the reduction of (IV) (15 g.) with zinc dust (6 g.) and glacial acetic acid (25 c.c.). The mixture was mechanically shaken for 5 hours and the filtrate nearly neutralised with Na_2CO_3 paste and extracted with ether, b. p. 118°/25 mm. (Found: Cl, 45·5. $C_4H_6O_2Cl_2$ requires Cl, 45·2 per cent).

αβ-Di-(β′-trichloro-α′-hydroxyethoxy)-γ-hydroxypropane (VI) was obtained by keeping a mixture of glycerol (25 g.), chloral (80 g.) and sulphuric acid (20 c.c.) overnight. The resulting mixture was washed with dilute methyl alcohol and extracted with chloroform, b.p. 145-50°/15 mm. (Found: Cl, 55·1. $C_7H_{10}O_5Cl_6$ requires Cl, 55·0 per cent).

Action of Nitric Acid on (VI).—A mixture of (VI) (30 g.) and concentrated nitric acid (70 c.c.) was kept at 0° for 12 hours. The mixture was diluted with water (15 c.c.) and the product (VII) separating on keeping for further 24 hours was recrystallised from methyl alcohol, m.p. 192-93°. (Found: Cl, 55·3; Equiv. 380. $C_7H_6O_5Cl_6$ requires Cl, 55·5 per cent. Equiv. 383).

Sodium Salt.—(Found: Na, 5·1; H_2O, 10·1. $C_7H_5O_5Cl_6Na$, $2\frac{1}{2}$ H_2O requires Na, 4·9; H_2O, 10 per cent). *Barium salt.*—(Found: Ba, 14·5; H_2O, 3·9. $C_{14}H_{10}O_{10}Cl_{12}Ba$, $2H_2O$ requires Ba, 14·7; H_2O, 3·8 per cent).

This action of nitric acid confirms the structure assigned to (VI).

Distillation of (VI) at 70 mm. pressure yields (VIII), b. p. 162-64°/25 mm. Yoder (*J. Amer. Chem. Soc.*, 1923, **45**, 476) obtained the compound by heating glycerol, chloral hydrate and zinc chloride under pressure. The *acetyl derivative* boils at 205°/120 mm. (Found: Cl, 40·2; $C_7H_9O_4Cl_3$ requires Cl, 40·4 per cent).

The nitrate of (VIII) (IX) separated after heating (VIII) with a mixture of nitric and sulphuric acids (2:1; 3 c.c.) for 2 minutes and keeping overnight. It crystallises from methyl alcohol in white needles, m.p. 64°. (Found: Cl, 40·1. $C_5H_6O_5NCl_3$ requires Cl, 39·9 per cent).

α-β-(β′-Trichloroethylidenedioxy)-γ-chloropropane (X) was prepared by the action of PCl_5 (equal weight) on (VIII). The reaction mixture was poured on to crushed ice and extracted with ether, b. p. 130°/15 mm. (Found: Cl, 58·9. $C_5H_6O_2Cl_4$ requires Cl, 59·1 per cent).

The methyl derivative of (VIII) was obtained by the action of dimethyl sulphate (equal weight) in the presence of 2*N*-alkali. The alkaline mixture was shaken for nearly 8 hours and the product extracted with ether, b. p. 140-42°/15 mm. (Found: Cl, 45·4. $C_6H_9O_3Cl_3$ requires Cl, 45·2 per cent).

(XII) was obtained from (VIII) on reduction with zinc dust and acetic acid. [See preparation of (V)], b. p. 160°/20 mm. (Found: Cl, 38·1. $C_5H_8O_3Cl_2$ requires Cl, 37·9 per cent). The acetyl derivatives (XIII) boils at 188°/30 mm. (Found: Cl, 31·2. $C_7H_{10}O_4Cl_2$ requires Cl, 31·0 per cent).

Di-αβ-(β′-trichloro-α′-hydroxyethyl)-ether of erythritol.—Erythritol (10 g.) and freshly distilled chloral (25 g.) were heated at 100° for 1 hour and the mixture diluted with water. The product is insoluble in the usual solvents in the cold and decomposes on heating in alcohol, ethyl acetate or glacial acetic acid. It was washed with warm dilute methyl alcohol and dried, m.p. 167-71°. (Found: Cl, 50·7. $C_8H_{12}O_6Cl_6$ requires Cl, 51·0 per cent). *The tetraacetyl derivative* was obtained by the action of acetic anhydride and a few drops of sulphuric acid. It separates from hot alcohol in cubic crystals, m.p. 164°. (Found: Cl, 36·2. $C_{16}H_{20}O_{10}Cl_6$ requires Cl, 36·4 per cent).

s-*Di(β-tribromo-α-hydroxyethoxy)-ethane.*—Ethylene glycol (5 g.) and bromal hydrate (25 g.) were heated for 1 hour at 130-40°. The liquid on dilution with water was extracted with ether, b.p. 145-47°/25 mm. (Found: Br, 77·0. $C_6H_8O_4Br_6$ requires Br, 76·9 per cent). The *diacetyl* derivative boils at 196°/135 mm. (Found: Br, 67·6. $C_{10}H_{12}O_6Br_6$ requires Br, 67·8 per cent).

β-Tribromoethylideneglycol.—A mixture of ethylene glycol (10 g.), bromal hydrate (25 g.) and concentrated sulphuric acid (10 c.c.) was kept for 3 days and the solid separating (18 g.) was crystallised from alcohol, m.p. 103-104°. The substance was also obtained by distilling dibromalglycol at ordinary pressure. It is stable towards hot alkalis. (Found: Br, 73·7. $C_4H_5O_2Br_3$ requires Br, 73·8 per cent).

αβ-Di(β′-tribromo-α′-hydroxyethoxy)-γ-hydroxypropane (XIV) (Formula similar to VI) was obtained as with the dibromal ethylene glycol, b.p. 205°/25 mm. (Found: Br, 73·5. $C_7H_{10}O_5Br_6$ requires Br, 73·4 per cent). The *triacetyl* derivative boils at 190°/155 mm. (Found: Br, 61·6. $C_{13}H_{16}O_8Br_6$ requires Br, 61·5 per cent).

αβ(β′-tribromoethylidene)-glycerol (XV) (Formula similar to VIII) was obtained by the distillation of (XIV) under reduced pressure, b.p. 210°/60 mm. (Found: Br, 67·5. $C_5H_7O_3Br_3$ requires Br, 67·6 per cent).

Tri-(β′-tribromo-α′-hydroxyethyl) ether of glycerol (XVI).—A mixture of glycerol (10 g.), bromal hydrate (35 g.) and concentrated sulphuric acid (10 c.c.) was kept for 2 days, diluted with water and extracted with ether. The product could not be distilled unchanged without decomposition under a pressure of 20 mm. (Found: Br, 76·6. $C_9H_{11}O_6Br_9$ requires Br, 77·0 per cent).

γ-(β′-Tribromo-α′-hydroxyethyl) ether of αβ-(β′-tribromoethylidene)-glycerol (XVII) was obtained by distilling (XVI) under reduced pressure, b.p. 145°/20 mm. (Found: Br, 75·2. $C_7H_8O_4Br_6$ requires Br, 75·4 per cent).

FIG. 1.

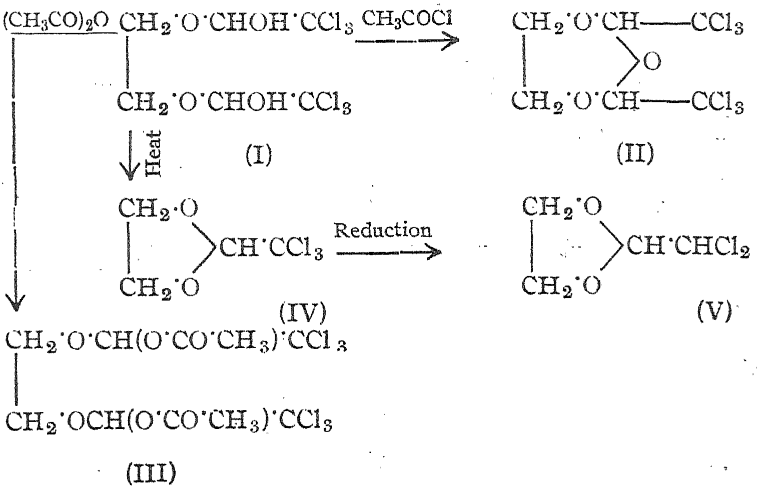
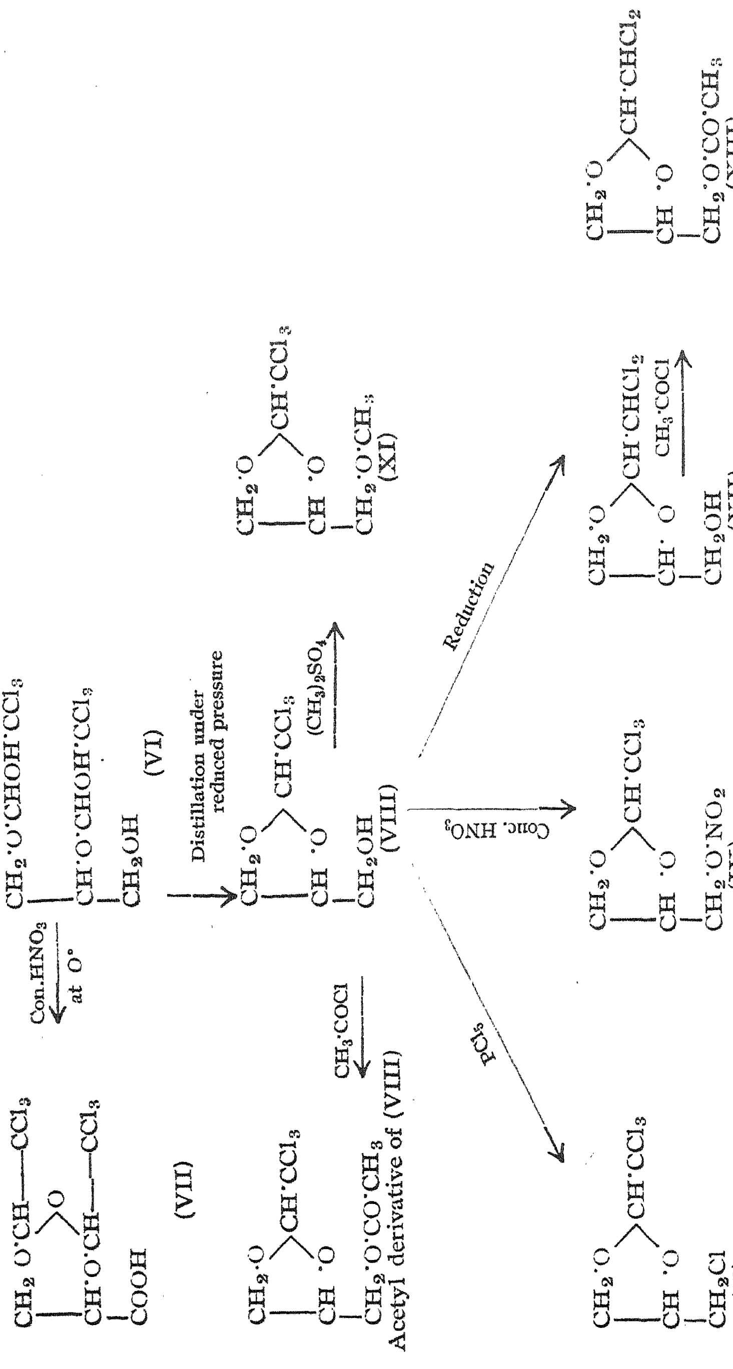


FIG. 2.



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An *X*-Ray Investigation of the Crystals of Benzoin.

BY MATA PRASAD AND JAGDISH SHANKER.

Benzoin (Ph·CO·CHOH·Ph) was prepared by refluxing a mixture of benzaldehyde (25 g. Merck's Extra Pure), KCN (2·5 g. Kahlbaum's Extra Pure), rectified spirit (31·5 c.c.) and water (25. c.c.) for about an hour. By this method pure benzoin was obtained which gave well developed small crystals after three crystallisations from alcohol, m. p. 134° (Groth, m. p. 134°).

The crystals are found to grow $a\{100\}$, $c\{001\}$, and $\sigma\{20\bar{1}\}$ with end faces $\omega\{11\bar{1}\}$. They belong to the monoclinic prismatic class and $a : b : c = 3{\cdot}4397 : 1 : 1{\cdot}8914$, $\beta = 106^\circ\ 50\frac{1}{2}'$ (*cf.* Groth, "Chemische Krystallographie," Vol. V., p. 199).

The crystals prepared as above were found to develop the $a\{100\}$, $c\{001\}$, $\sigma\{20\bar{1}\}$ and $\omega\{11\bar{1}\}$ faces and sometimes (101). They were examined by the rotating crystal method using *k*-copper radiations from a Shearer gas tube. The rotation photographs about the three axes (Figs. 1, 2 and 3) gave the following dimensions for the unit cell

$$a = 18{\cdot}75\text{Å}, \quad b = 5{\cdot}72\text{Å}, \quad c = 10{\cdot}46\text{Å}, \quad \beta = 106^\circ\ 50\tfrac{1}{2}'$$

A rotation photograph was also taken about an axis perpendicular to the *b*-axis in the (101) plane. The length of the axis was found to be 24·05Å which agrees with the calculated value 23·97Å. The axial ratio is $a : b : c = 3{\cdot}28 : 1 : 1{\cdot}83$ which agrees fairly well with that given above.

TABLE II.

General planes.

111 v. s.	$11\bar{1}$ v. s.	312 m.	$31\bar{2}$ m.,w.m.	522 m.,w.m.	... ...
112 m s.	$11\bar{2}$ m. s.	313 m. s.	$31\bar{3}$ w. m.	... ...	$52\bar{3}$ w.
113 w. m.	$11\bar{3}$ w. m.	314 w.m.,w.	$31\bar{4}$ w.	611 m.	$61\bar{1}$ m. s.
121 s.,m.s.	$12\bar{1}$ s.,m.s.	321 w. m.	$32\bar{1}$ w.m.,h.	612 m.	$61\bar{2}$m.
122 w m.	$12\bar{2}$ w.	322 m.	... ...	614 m.	$61\bar{4}$ m. m.
123 w.	123 w.	$\left.\begin{matrix}324\\423\end{matrix}\right\}$ m.	$32\bar{3}$ v. w.	621 w. m.	$62\bar{1}$ w.
124 v. w.	... ...	411 s.	$41\bar{1}$ m. s.	... ...	$62\bar{2}$ m.,w.m
211 m.	$21\bar{1}$ m.	412 m.	$41\bar{2}$ w. m.	623 m.,w.m.	$62\bar{3}$ w. m.
212 m. s.	$21\bar{2}$ m.	413 m.	$41\bar{3}$ w. m.	711 w.	... ...
213 s.	$21\bar{3}$ m.	414 w. m.	$41\bar{4}$ w. m.	712 m.	$71\bar{2}$ w. m.
214 w.	$21\bar{4}$ m.	421 m.	$42\bar{1}$ w.	713 w. m.	$71\bar{3}$ w.m.,w.
221 m.	$22\bar{1}$ s.	422 m. s.	$42\bar{2}$ m.	... ...	$71\bar{5}$ v. w.
222 m. s.	$22\bar{2}$ v. w.	423 w.m.,w.	$42\bar{3}$ m.	721 w.	$72\bar{1}$ w. m.
223 w.	$22\bar{3}$ v. w.	424 m.	... ...	... ...	$72\bar{2}$ w. m.
$\left.\begin{matrix}224\\324\end{matrix}\right\}$ w.	... ...	512 m. s.	$51\bar{2}$ m.	811 m.	$81\bar{1}$ m.
311 s.	$31\bar{1}$ m.	513 w.	... ...	812 m.	$81\bar{2}$ w.
		521 w. m.	$52\bar{1}$ w. m.	813 m.	$81\bar{3}$ m.
				821 w.	... ...
				913 w. m.	$91\bar{3}$ w.

It will be seen from the above list of planes that (hol) planes are halved when h is odd. Further (oko) planes have not appeared at all. This shows that these planes are very weakly reflecting. It is, therefore, probable that (010) is halved and (020) being very weak has not appeared. The crystals may, therefore, belong to the space group C_{2h}^{5} (*cf.* Astbury and Yardley, *Phil. Trans.*, 1924, **A**, **224**, 221).

This is more likely since a large number of organic crystals belonging to the monoclinic prismatic class belong to this space group. The number of molecules in the unit cell required by the space group is four and that calculated from the dimensions of the unit cell and the density of the crystals (found to be $=1{\cdot}310$) is

$$n=\frac{abc \sin \beta \times \rho}{M \times 1{\cdot}66}=3{\cdot}997=4 \text{ (approx.)}$$

This shows that the molecules in the cell are asymmetric.

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Viscosity of Thorium Phosphate Gel-forming Mixtures during Gelation.

By S. M. MEHTA, M. U. PARMAR AND MATA PRASAD.

Viscosity measurements have often been used for studying the processes involved in the formation of gels (*cf. J. Indian Chem. Soc.*, 1935, **12**, 552). These measurements have been made during the gelation of gelatine solutions prepared under different conditions by Levites (*Z. Chem. Ind. Kolloide*, 1908, **2**, 208), Schroeder (*Z. physikal. Chem.*, 1903, **45**, 75), Gokun (*Kolloid Z.*, 1908, **3**, 84), Shoji (*Biochem. J.*, 1919, **13**, 227) and others who obtained smooth curves for the variation of the viscosity of these solutions with time. Levites found that the rate of increase of viscosity is nearly proportional to time while Shoji concluded that the viscosity-time curves in the early stage of gelation are represented by the equation

$$\eta - \eta_1 = \frac{\mu t}{1 + \frac{\mu t}{\lambda}}$$

where μ and λ are constants.

Mardles (*Trans. Faraday Soc.*, 1923, **18**, 327) also found smooth viscosity-time curves during the gelation of a sol of cellulose acetate in benzyl alcohol and they could be represented by the formula,

$$\eta - \eta_0 = ae^{kt}$$

where η is the apparent viscosity of the gel-forming sol after an interval of time t, η_0, the original viscosity of the sol, and k, the rate of gelation. Heymann (*Trans. Faraday Soc.*, 1935, **31**, 846), however, found that the viscosity of methyl cellulose during the sol-gel transformation decreased with time regularly if the sol was aged at 44° but if the ageing took place at higher temperatures, the viscosity first decreased and then increased to a higher value.

Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 390) measured the viscosities of the gel-forming mixtures of various inorganic jellies during gelation and found that there are three distinct stages in the formation of gels. In the first stage there is very little change in viscosity with time and this corresponds to the passage of the crystalloidal substance to the colloidal state; in the second the regular exponential change in viscosity with time corresponds to the gradual neutralisation of the charge on the micelles with consequent increase in hydration; in the third stage there is a sudden rise in viscosity due to the formation of specific structures. Prasad, Mehta and Desai (*J. Phys. Chem.*, 1932, **36**, 1384) measured the viscosity during the formation of silicic acid gels and found that it increased regularly with time and that the viscosity-time curves were continuous. Their observations showed that the passage of crystalloidal silicic acid into colloidal state, the coagulation of colloidal silicic acid and the formation of specific structures form a single continuous process.

These authors (*J. Phys. Chem.*, 1932, **36**, 1391) also found that non-electrolytes accelerate the rate of change in viscosity of the alkaline mixtures while they retard that of the acidic ones and further that an increase in the amount of the non-electrolytes in the mixtures increases the acceleration or retardation of the rate of change in viscosity. Levites (*Z. Chem. Ind. Kolloide*, 1908, **2**, 237) observed that non-electrolytes retard the sol-gel transformation of gelatine and agar agar.

In the present investigation the viscosity of thorium phosphate gel-forming mixtures has been determined under different conditions during the progress of gelation. The effect of the variation of concentration of thorium nitrate and phosphoric acid as well as of the addition of electrolytes and non-electrolytes on the rate of change of viscosity has been examined.

EXPERIMENTAL.

The method as well as the apparatus used for measuring viscosity were those previously described by one of us (*J. Indian Chem. Soc.*, 1935, **12**, 552; *Bom. Univ. J.*, 1935, **4**, 46).

Solutions of thorium nitrate and phosphoric acid were prepared from Kahlbaum's extra pure chemicals whose purity was tested before use. The concentrations of the solutions were 6% and 2*N*, respectively. A known amount of thorium nitrate solution was taken in a test tube and a known amount of the solution of phosphoric acid together with sufficient distilled water to make up the total volume of the mixture to 10 c.c. was taken in another test tube and the two were kept in a thermostat to attain a constant temperature. On mixing the two solutions a slight precipitate was obtained, which disappeared on shaking the mixture. It was then introduced into the viscometer and suction at 15 cms. pressure of water, which was kept constant throughout the investigation, was applied. The gel-forming mixture remained transparent throughout the process of gelation.

The results obtained with mixtures containing different amounts of thorium nitrate and phosphoric acid are similar in nature. Only one of these results is shown in the following table in which η represents the viscosity at time T.

TABLE I.

Thorium nitrate = 0·48 g. Phosphoric acid = 0·12 N.

T ...	8′ 27″	18′ 47″	22′ 51″	26′	31′ 14″	42′ 51″
$\eta \times 10^5$ ...	1279	2223	2452	2816	3465	5076
T ...	49′ 22″	57′ 49″	72′ 11″	82′ 21″	96′ 52″	
$\eta \times 10^5$ ...	6198	7932	11470	13030	16240	

The viscosity of mixtures containing (*i*) a fixed amount of thorium nitrate and different amounts of phosphoric acid and (*ii*) fixed amount of phosphoric acid and different amounts of thorium nitrate, at different intervals of time is shown in Figures 1 and 2.

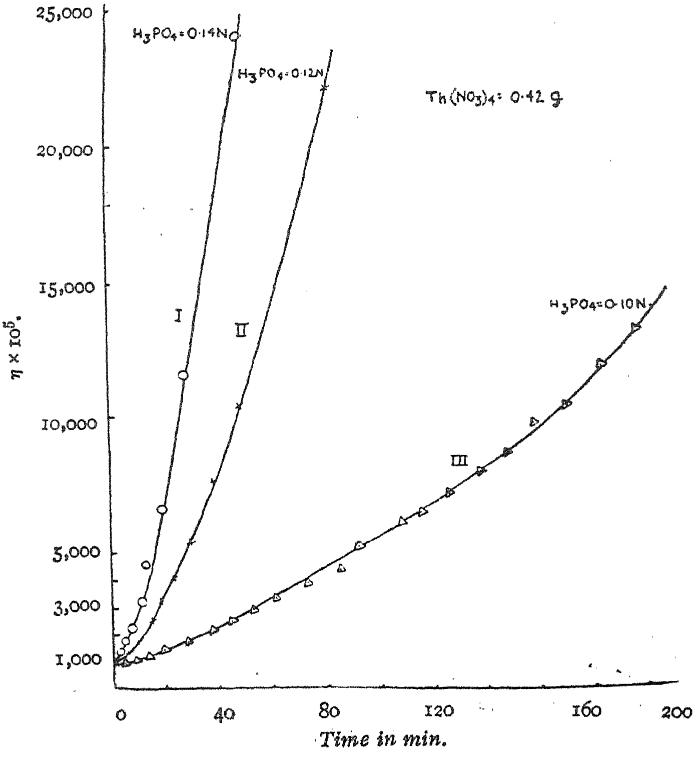
Effect of Non-electrolytes.—The effect of methyl, ethyl and *n*-propyl alcohols, acetone, glycol and glycerine on the viscosity of thorium phosphate gel-forming mixtures was investigated. Various quantities of these non-eleclolytes were added to phosphoric acid solution to which sufficient distilled water was added to make the total volume of the gel-forming mixture 10 c.c. The nature of the results obtained is similar with all the non-electrolytes used, and is shown in Fig. 3 for ethyl alcohol which also shows the effect of the addition of increasing amounts of the non-electrolytes.

Effect of Electrolytes.—The effect of hydrochloric, nitric, sulphuric acids and of sodium chloride was investigated. The results with acids are shown in Fig 4 and those with sodium chloride in Fig. 5.

DISCUSSION.

It appears from the curves (Figs. 1 and 2) that after mixing the gel-forming constituents, the viscosity increases at first slowly for some time and later on the rate of increase becomes very rapid. The continuous nature of the viscosity-time curves indicates that the colloidal particles in the mixture grow gradually to bigger dimensions and no sharp changes in their rate of aggregation and hydration take place during gelation. The three stages in the process of gel-formation found by Satya Prakash and Dhar *(loc. cit.)* from viscosity measurements are not obvious in the formation of thorium phosphate gels. Curves of log (η_s-η_0), where η_s and η_0 (η_0 refers to the extrapolated value of the viscosity from η-t curves at 0 time) are the viscosities of the mixtures and water, respectively, plotted against log t (Fig. 6) from the curves of I, II, and III (Fig. 1) and IV and VII (Fig. 2) are straight lines with no breaks. This leads to the conclusion that the various stages involved in the setting of a gel, such as the formation of the colloidal particles, their hydration and coalescence and the acquiring of specific structures, altogether form one continuous process. It is important to note that the periodic nature of the viscosity-time curves obtained by previous workers (*J. Indian Chem. Soc.*, 1933, **10**, 329, 589; 1934, **11**, 173; 1935, **12**, 552)

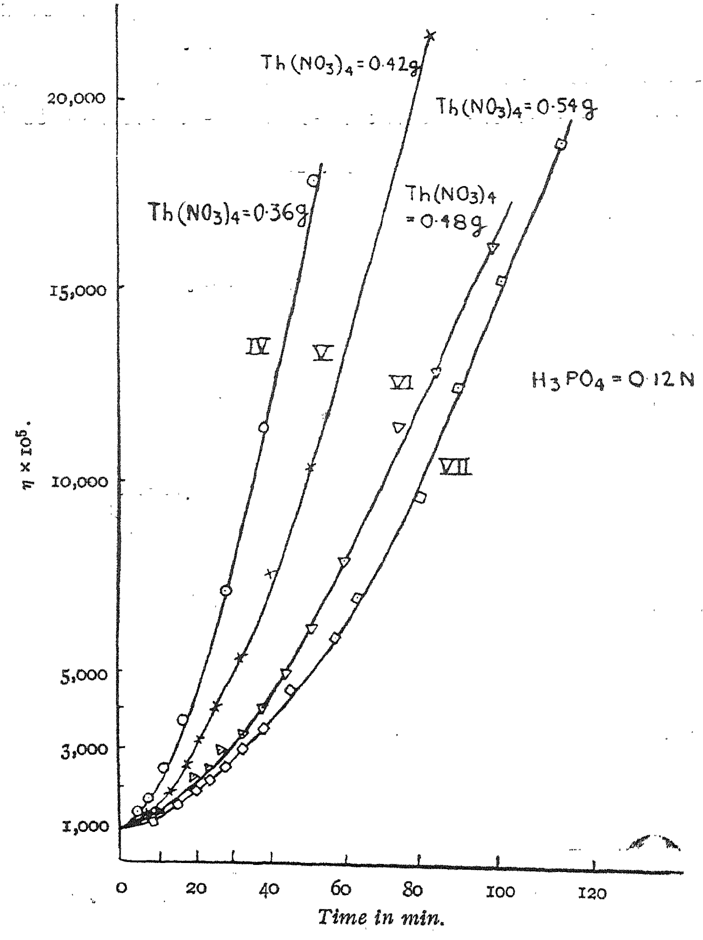
FIG. 1.



is not observed in the case of changes of viscosity of gel-forming mixtures. It is probable that the periodic or discontinuous nature of viscosity-time curves is to be expected only in the case of lyophobic sols or in those cases where sedimentation takes place.

With an increase in the amount of phosphoric acid, the rate of change in viscosity increases fairly rapidly as will be seen from the rapid increase in the steepness of the curves (Fig. 1). This may be due to an increase in (*i*) the number of micelles in unit volume or (*ii*) their size and their degree of hydration, or (*iii*) both. The first factor does increase as the amount of phosphoric acid in the gel-forming mixture is increased. But as all the mixtures were quite transparent after mixing and remained so till they set, there is no

FIG. 2.



direct evidence to show that the size of the micelles is considerably increased by increasing the amount of phosphoric acid in the mixture.

On increasing the amount of thorium nitrate in the gel-forming mixtures, the rate of change in viscosity decreases and the viscosity-time curves (Fig. 2) become less steep. This is due to the fact that thorium ions peptise thorium phosphate and thus increase the degree of dispersity of the micelles. This effect decreases rapid changes in

FIG. 3.

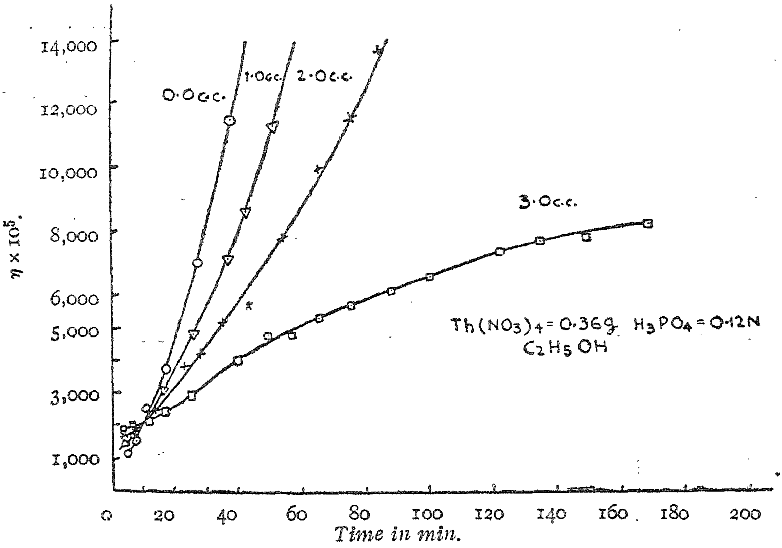
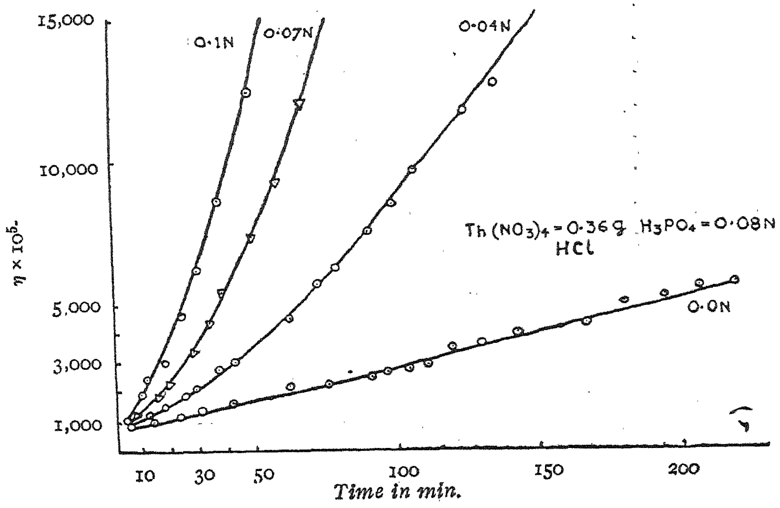


FIG. 4.



viscosity; it also increases the density of charge on the micelles and thereby diminishes their rate of hydration which again decreases the rate of change in viscosity (*cf.* Dhar, *J. Phys Chem.*, 1925, **29**, 1566). From the transparency of all the gels studied herein, it appears that the degree of hydration of the micelles is very great and plays an important part in affecting changes in the viscosity of the gel-forming mixtures.

The addition of non-electrolytes (*cf.* Fig. 5) decreases ths rate of change in viscosity. In the earlier stages (for about 15 to 20 minutes) the viscosity of the mixture increases but later on it decreases as the amount of the non-electrolytes in the mixture is increased. The first increase may be due to the formation of bigger particles of the precipitate of thorium phosphate which has a tendency to seperate out due to a decrease in its solubility in non-electrolyte-water mixtures, more so as larger quantities of non-electrolytes are added to the mixture. This explanation is supported by the fact that in the case of alcohols and acetone a slight precipitate separated out just after mixing and disappeared after sometime. No such seperation of any precipitate was observed in the case of glycol and glycerol.

FIG. 5.

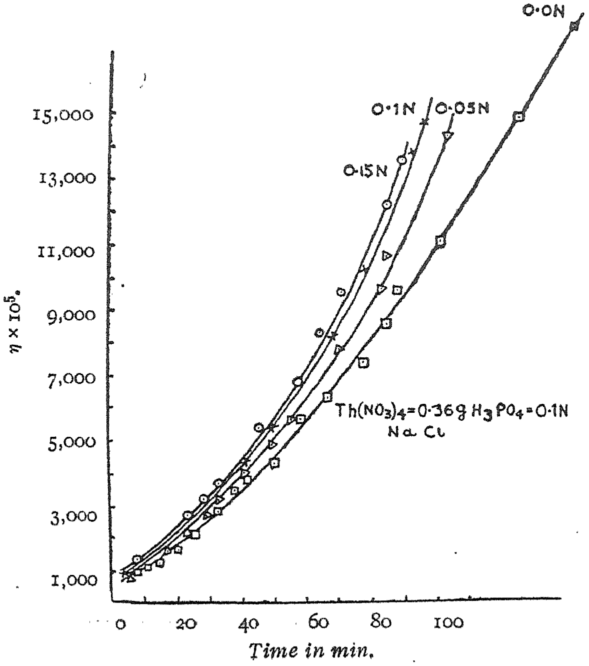
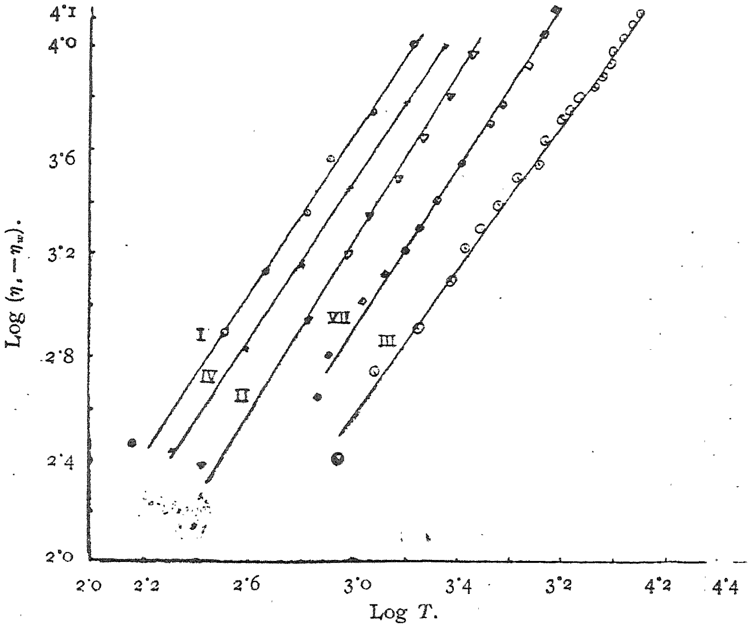


FIG. 6.



Curves I—III taken from curves in Fig. 1 and IV & VII from those in Fig. 2.

The behaviour of non-electrolytes can be explained on the suggestion of Prasad and Hattiangadi (*J. Indian Chem. Soc.*, 1929, **6**, 991) that non-electroclytes increase the density of charge on positively charged sols. Consequently in accordance with Dhar's views the degree of hydration of colloidal particles decreases and hence the rate of change in viscosity of the gelling system is decreased.

The addition of acids and sodium chloride (*cf.* Fig. 6) increases the rate of change in viscosity with time. This is in agreement with the usual effect of electrolytes that they decrease the density of charge on colloidal particles and thereby the degree of hydration of the particle and the rate of change in viscosity of the gelling system are increased. But it has been found that H-ions are very effective in peptising thorium phosphate. Hence when lower concentrations of the acids are employed, the density of charge on the colloid particles increases and the lowering in the rate of viscosity is observed.

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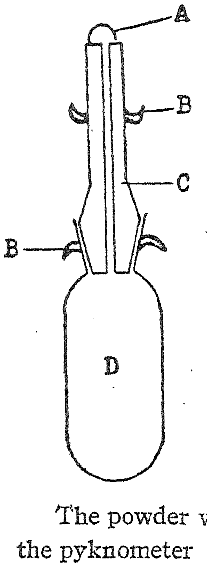
Immersion Pyknometer.

By Walter Jung.

The hydrostatic method of estimating the specific gravity of solids offers no difficulty so long as the estimation of a large piece of solid is concerned but is not convenient for coarse grains and fine powders usually met with in technical practice. In the following is described a form of the pyknometer called the immersion pyknometer which allows the density determinations, especially of powders to be made accurately and easily.

The immersion pyknometer (see Figure) is made of glass or quartz. It contains an empty vessel (D) of about 1 to 10 c.c. capacity, in which a capillary tube (C) is well ground in. This capillary tube and the vessel carry glass (or quartz) hooks (B) from which are hung two V_2 A springs. The ground joint is not, therefore, greased and allows the apparatus to be used with organic substances. The capillary also carries a glass or quartz hoop (A) to which a thin platinum wire could be stuck. While weighing under immersion, the instrument is hung with the help of the wire so that always a constant length of it is under the liquid.



Before use, the apparatus is washed with pure alcohol and ether and dried in vacuum.

The powder whose density is to be determined is weighed out in the pyknometer itself in air and then in water. The substance is covered with air-free distilled water. The pyknometer vessel is placed in a vacuum desiccator and all the air is sucked out. Then, through a connection to a flask of the air-free distilled water, the desiccator is gradually filled with water till the pyknometer is also filled. The pyknometer is taken out, wiped dry and weighed under water at a constant temparature. Then

$$s = \frac{(p_2 - p_1)}{(p_2 - p_1) - (p_3 - p_4)}$$

where s denotes the density of powder, p_1, the wt. of empty pyknometer, p_2, wt. of pyknometer with substance, p_3, wt. under water of the pyknometer with substance and p_4, the wt. under water of empty pyknometer.

The following table shows the accuracy of the instruments into four different powders. These powders are those usually met with in ceramic works.

TABLE I.

Temperature=16°..

(a)	(b)	(c)	(d)
s=2·509	s=2·494	s=3·837	s=2·865
2·509	2·494	3·837	2·865
2·509	2·493	3·837	2 865
2·509	2·494	3·838	2·865

The immersion pyknometer can also be used with any liquid other than water, whose specific gravity is known, and which does not necessarily dissolve the solid.

In this case, p_3 and p_4 would represent the weights under the liquid of density σ instead of water. Then the density of solid

$$s = \frac{(p_2-p_1)\sigma}{(p_2-p_1)-(p_3-p_4)}.$$

Immersion pyknometer can also be used for the determination of the density of liquids in a very elegent way. The pyknometer is used as an immersion body as in the case of Mohr-Westphal balance. The dsnsity of liquid is given by

$$\sigma = \frac{p_1-p_2}{p_1-p_3}.$$

I wish to express my best thanks to Prof. Dr. Ludwig Wolf for the great interest he has taken in this work and to Dr. B. S. Srikantan for kindly translating this paper into English.

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Complex Compounds of Iridium. Part IV.

By Prafulla Chandra Rây and Nripendra Nath Ghosh.

The action of ammonia on $IrCl_3 \cdot 3Et_2S$ (yellow variety) at 140° and the consequent formation of $IrCl_3 \cdot Et_2S \cdot 2NH_3$ and $(IrCl \cdot 5NH_3)Cl_2$ have already been described (Rây and Ghosh, *J. Indian Chem. Soc.*, 1934, **11**, 517). The mother liquor from these Ir-ammines on concentration over sulphuric acid in vacuum and subsequent treatment with alcohol, gave extremely hygroscopic precipitate which could not be further examined. Attempts to prepare the corresponding nitrate by treating the mother liquor with silver nitrate solution, led to no better results. On the other hand, treatment with hot silver sulphate solution resulted in the isolation of a sulphate of the formula $(Ir \cdot Et_2S \cdot 5NH_3)_2 (SO_4)_3, 2H_2O$. The sulphate radicals were found to be ionisable and completely precipitable by barium chloride. Determination of molecular conductivity gave, however, abnormally high values due probably to partial hydrolysis. From the formation of the above sulphate, it may be concluded that the mother liquor of the ammines, contains a chloride having the formula $(Ir \cdot Et_2S \cdot 5NH_3)Cl_3$.

But the action of ammonia on $IrCl_3 \cdot 3Et_2S$ (yellow variety) simply at the temperature of the water-bath produced a new Ir-ammine ($IrCl_3 \cdot 2Et_2S \cdot NH_3$)—only one Et_2S being replaced by ammonia—along with a small amount of the products formed at higher temperatures (*cf.* Rây and Ghosh, *loc. cit.*).

By the action of ethyl sulphide on ammonium chloroiridate, three compounds (A) $IrCl_3 \cdot 3Et \cdot S$ (yellow), (B) $IrCl_{32} \cdot 3Et_2S$ (red) and (C) $Ir_2Cl_5 \cdot 4Et_2S$, have been obtained, of which (A) and (B) have been described to be geometrical isomers (Rây and co-workers, *ibid.*, 1932, **9**, 251; 1933, **10**, 275). The red crystals of the compound (B) freshly isolated from chloroform has been found to contain one molecule of chloroform of crystallisation which it gives up spontaneously at the ordinary temperature and in course of a quarter of an hour, becomes reddish-white and opaque like an efflorescent compound. The reddish white mass has been found, on analysis, to correspond with the compound (B). The melting points of the red crystals and the reddish white mass are identical due evidently to the rapid and spontaneous loss of the chloroform of crystallisation. Although the chloroform of crystallisation is present in several organic compounds, *e.g.*, the condensation product of leuconic acid with tolylene diamine chloroform being expelled at 140° (*Ber.*, 1886, **19**, 776), methyl-ethyl-allylphenylammonium iodide (*Ber.*, 1903, **36**, 3795), etc , its presence is rather rare with inorganic and organometallic compounds. It should, however, be pointed out that during crystallisation of the compound (B) from chloroform, a small fraction is always transformed into (A), *i.e* , the yellow variety.

The action of bases on the compound (B) will form the subject of our next communication.

EXPERIMENTAL.

Preparation of $(Ir\cdot Et_2S\cdot 5NH_3)_2(SO_4)_3$, $2H_2O$.—$IrCl_3\cdot 3Et_2S$ (2·5 g.) was heated in a sealed tube with liquor ammonia (18 c.c.) first on a water-bath for three hours and finally in the bomb-furnace at 130°-140° for 3 hours. Ethyl sulphide replaced by ammonia was extracted with ether. From the main solution $IrCl_3\cdot Et_2S\cdot 2NH_3$ and $(IrCl\cdot 5NH_3)Cl_2$ were obtained and a viscous liquid remained, which was not crystallisable and was treated with hot solution of silver sulphate till complete precipitation was effected. Silver chloride, thus precipitated, was removed by filtration. The filtrate decomposes at the temperature of water-bath and was hence concentrated in vacuum over sulphuric acid. The concentrated solution, thus obtained, was treated with alcohol in order to precipitate the compound. The process of precipitation was repeated thrice by dissolving the precipitate in the least possible quantity of water each time, and the compound was finally crystallised from moist acetone It is hygroscopic and contains two molecules of water of crystallisation. [Found: N, 12·98, 13·12; S, 13·8; Ir, 36·93, 35·81. $(Ir\cdot Et_2S\cdot 5NH_3)_2(SO_4)_3$, $2H_2O$ requires N, 13·21 ; S, 15·09; Ir, 36·41 per cent).

Determination of Ionisable Sulphate of $(Ir\cdot Et_2S\cdot 5NH_3)_2(SO_4)_3,2H_2O$.

(*i*) *Precipitation method.*—A certain amount of the above substance was treated with cold barium chloride solution. Barium sulphate was precipitated. [Found: SO''_4, 26·63. $(Ir\cdot Et_2S\cdot 5NH_3)_2(SO_4)_3$, $2H_2O$ requires (if three SO_4'' be ionisable) SO_4'', 27·17 per cent].

(ii) Molecular conductivity Measurement.

Mol. conc. (*M*)	0·01	0·005	0·0025	0·00125	0·000625	0·000312
Mol. conducty.	322	364	408	466	532	585

(Molecular conductivity of alumium sulphate at infinite dilution is 373).

Preparation of $IrCl_3{\cdot}2Et_2S{\cdot}NH_3$.—$IrCl_3{\cdot}3Et_2S$ (3 g.) (yellow variety) was heated on a water-bath in a sealed tube with liquor ammonia (18 c.c.) with occasional shaking, till all the $IrCl_3{\cdot}3Et_2S$ went into solution. About 20 hours' heating was required. When cold, an orange-yellow crystalline substance and a yellew solution with a layer of ethyl sulphide floating over it, were obtained. The orange-yellow crystalline substance was isolated and recrystallised from hot water, m.p. 155°. (Found: Cl, 21·1; S, 12·92; Ir, 38·95, 39·0. $IrCl_3{\cdot}2Et_2S{\cdot}NH_3$ requires Cl, 21·45; S, 12·88, Ir, 38·87 per cent). From the main solution, other Ir-ammines were obtained.

Preparation of $IrCl_3{\cdot}3Et_2S$, $CHCl_3$—Ethyl sulphide (5 c.c.) was added to ammonium chloriridate (5 g.) in water (300 c.c.) and alcohol (30 c c.) and it was heated on a water bath (80°) for 12 hours, when a substance gradually separated out, the colour of the solution changing from deep red to yellowish red. The substance, thus separated, was isolated and extracted repeatedly with hot benzene in order to remove $IrCl_3{\cdot}3Et_2S$ (yellow variety); a residue remained, which on treatment with chloroform, gave a deep red solution from which red transparent crystals were obtained. These crystals turned on reddish-white opaque mass within a quarter of an hour, m.p. 171°. (Found:Cl, 31·1; S, 13·67, 14·0; Ir, 28·0, 28·1. $IrCl_3{\cdot}3Et_2S$, $CHCl_3$ requires Cl, 30·9; S, 13·9; Ir, 28·0 per cent).

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Studies in the Coagulation of Colloids. Part XI. Variation of Optical Refractivity during the Coagulation of Colloid Manganese Dioxide and new Evidence for the Discontinuity of the Change.

By Shridhar Sarvottam Joshi and S. Jaya Rao.

Previous studies in these series (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329; Joshi and Menon, *ibid,*, 1933, **10**, 599; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133; Joshi and Iyengar, *ibid.*, 1934, **11**, 555, 573; Joshi and Panikkar, *ibid.*, 1934, **11**, 797; also *J. chim. Phys.*, 1935, **32**, 455-459; *Proc. 'Acad. Sci., U. P.*, 1935, **5**, 41-45) have largely dealt with the results of viscosity measurements during the coagulation of a number of sols by various electrolytes, especially in the *slow* region. One outstanding result of these investigations has been to demonstrate that failure to recognise the possible discontinuity in time of the progress of a coagulation especially in the *slow* region constitutes the chief deficiency in the current theories of the kinetics of the change as developed by Smoluchowski (*Z. physikal. Chem.*, 1917, **92**, 129), Freundlich ("Colloid and Capillary Chemistry," 1926, pp. 442-450) and others. In order to obtain more information about the factors responsible for the break down of these theories, it was thought instructive to examine the change by use of a method for measuring coagulation, different from the ones employed previously (*loc. cit.*; *cf.* also, Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, **8**, 11, 337; Joshi and Phansalkar, *ibid.*, 1932, **9**, 157; Joshi and Lal, *ibid.*, 1933, **10**, 61). A reference to the literature of the subject showed that a change in the refractive index does not appear to have been used as a measure of the corresponding degree of coagulation. From the very beginning of work in this line (*cf.* Joshi and Godbole, *Proc. Ind. Sci. Congress*, 1931, p. 135; especially, *cf.* Joshi and Jaya Rao, *ibid.*, 1934, p. 210; also, Joshi and Panikkar, *ibid.*, p. 213) was realised the marked convenience and sensitivity of this method. Of this, the experiments on colloid maganese dioxide (*cf.* also Joshi and Lal, *loc. cit.*) now to be described, would appear to be the first detailed application in the field of coagulation kinetics.

EXPERIMENTAL.

The sol was prepared by adding slowly concentrated ammonia, a few drops at a time, to a boiling solution of potassium permanganate. The excess of ammonia was boiled off after failing to note any traces of the permanganate in a given sample of the sol after coagulation with barium chloride. The sol thus prepared contained potassium hydroxide in small amounts which is produced in the interaction between ammonia and permanganate (Cuy, *J. Phys. Chem.*, 1921, **25**, 415 ; *cf.* also Joshi and Narayan, *J. Indian Chem. Soc.*, 1930, **7**, 883); with this residual amount of alkali, the stability of the colloid was found to be very satisfactory. The colloid was stocked in silica vessels. Its content was estimated by the addition of a known volume of standard oxalic acid acidified with sulphuric acid, and the titration of the excess with standard permanganate. The colloid content was kept constant at 2·06 g. MnO_2 per litre in the coagulating mixture in all these experiments.

The refractive index was determined for the sodium light with a Pulfrich refractometer capable of giving results correct to the fifth decimal place. One c.c. of the colloid preheated to 30° was introduced into the cell of the refractometer which was brought previously to the above temperature. The concentration of the coagulator was adjusted by preliminary experiments so that a measurable change in the refractive index was produced during about 2-3 hours at least. An equal amount of the electrolyte solution preheated as above was then carefully added to the colloid and the mixture stirred twice. Measurement of the refractive index was then started; it was discontinued when (*i*) the mixture showed a constant refractivity over an appreciably long period, (*ii*) or, the coagulating mixture became too opaque to let any light through, (*iii*) or, the coagulation had advanced so far as to produce optical heterogeneities due to particles of the coagulum in the cell of the refractometer. In view of the fact that but small percentage changes in the refractive index were produced during any of the coagulations studied in these experiments, the susceptibility of this quantity to temperature variations, and also the sensitivity of the instrument used, control of the temperature was found to be an important factor in order to yield accurate and reproducicble results. This was kept constant at 30°, the utmost fluctuations being within 1/20° to 1/10°, except during experiments referred to in curve 1 in Fig. 6 showing the influence of the temperature on the refractive index of the colloid. This constancy of temperature was more than that required for the purpose of this work (*vide infra*). These results are shown by refractive index—time curves in Figs. 1-5. In order to facilitate comparison, the same scale, (*viz*. one unit on the abscissa = 10 minutes, and one on the ordinate = 0·00050 change in μ, the refractive index, except in curves 1, 2 in

FIG. 1.

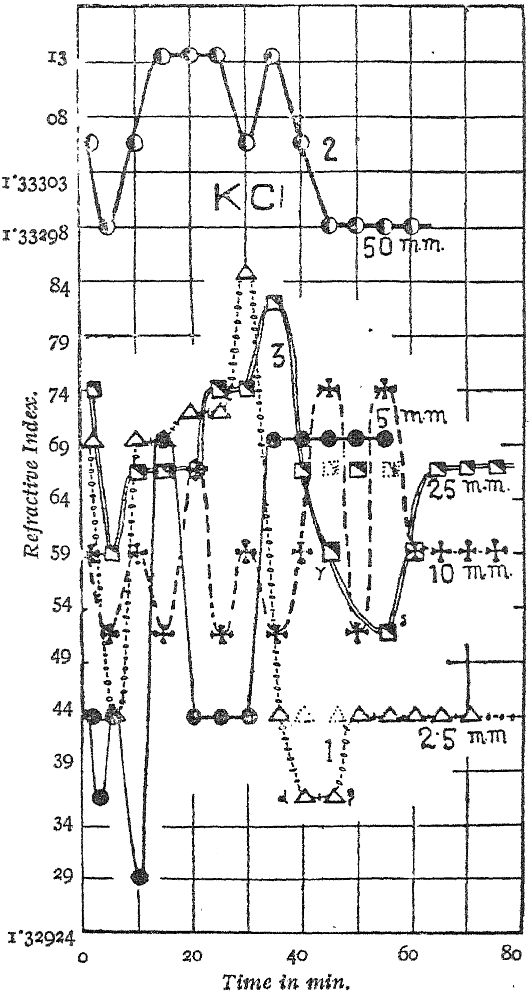


Fig. 4) has been employed in all the figures. The origin for any one of a family of curves has shifted along the ordinate to prevent neighbouring curves from coalescing. This also served appreciably to economise space in the figures. Curves in Fig. 1 give μ—time curves when the coagulator concentration was varied in the range 2·5 to 50 m. mols of potassium chloride in the coagulating mixture. This and the next, Fig. 2, show data for the so-called lyotropic series (HCl, Li_2SO_4, NaCl, KCl and NH_4Cl). Results with strontium chloride and lanthanum nitrate are shown in Fig. 3. Aluminium chloride (*cf.* Fig. 4) behaved differently from lanthanum nitrate although both are trivalent. Only a few typical results with a tetravalent coagulator, *e.g.*, thorium nitrate are shown in Fig. 5. Experiments were also made with different concentrations of cerium nitrate. These curves were found to be essentially similar to those due to thorium nitrate, and so have not been shown. For the same reason, curves with a number of barium chloride (*cf.* Fig. 3) concentrations, as also those corresponding to varying colloid contents and different amounts of potassium chloride used as a coagulant (*cf.* Fig. 1) have been deleted. Curves 1 and 2 in Fig. 6 show respectively the influence of temperature and of the colloid content on the refractive index of the sol used in this work.

DISCUSSIONS.

The information available in the literature in regard to the optical refractivity of the colloid state during its characteristic changes is markedly insufficient in respect of data and theory. Walpole (*Kolloid Z.*, 1913, **13**, 241), who was perhaps the first to work in this line, studied the influence on the refractive index of aqueous gelatine of (*i*) the addition of the chloride, sulphate and thiocyanate of ammonia, of hydrochloric acid and sodium hydroxide, (*ii*) changing the temperature and the concentration, and (*iii*) transition from the sol to the gel condition. He found that the changes in μ, the refractive index were related linearly to the corresponding densities. Wintgen (*ibid.*, 1921, **28**, 5) confirmed this from observations with colloid arsenious and antimony sulphides, silicic and molybdic acids, ferric hydroxide and tanin. The recent accurate work of Boutaric and co-workers (*Compt. rend.*, 1927, **185**, 892; *Rev. gen. Colloid*, 1927, **5**, 658) using an interference refractometer has shown that the difference between the refractive index of the sol and that for the medium is proportional to the colloid content. Data on colloid manganese dioxide shown by curve 2, Fig. 6 show that μ varies linearly with respect to colloid content as observed by the above workers. At very low proportions of the dispersed phase, however, it is seen that μ rises almost insensibly by increasing the colloid content of the sol. Similar results (to be published shortly) were obtained by Mr. G. R. Godbole in these laboratories in the case of colloid arsenious sulphide. Curve 1 in Fig. 6 show that μ diminishes linearly by increasing the temperature;

FIG. 2.

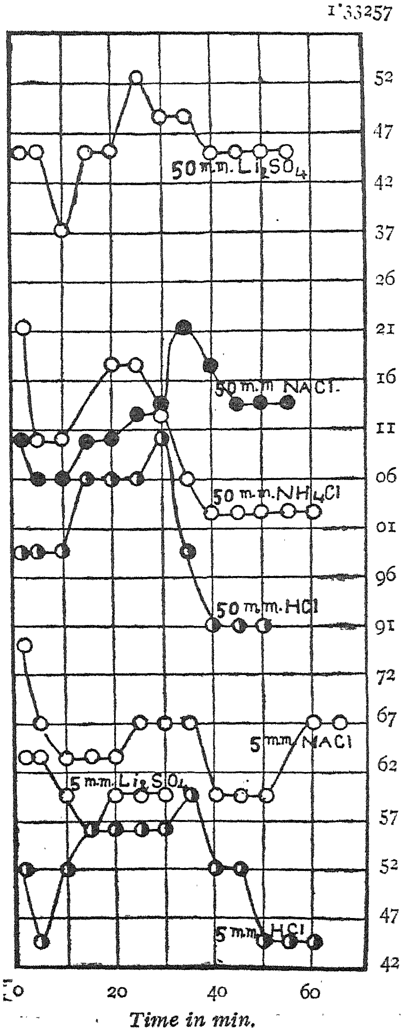
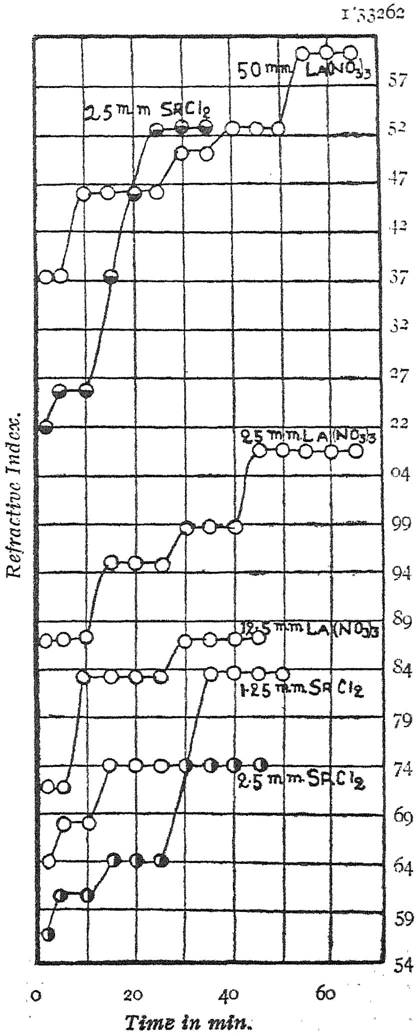


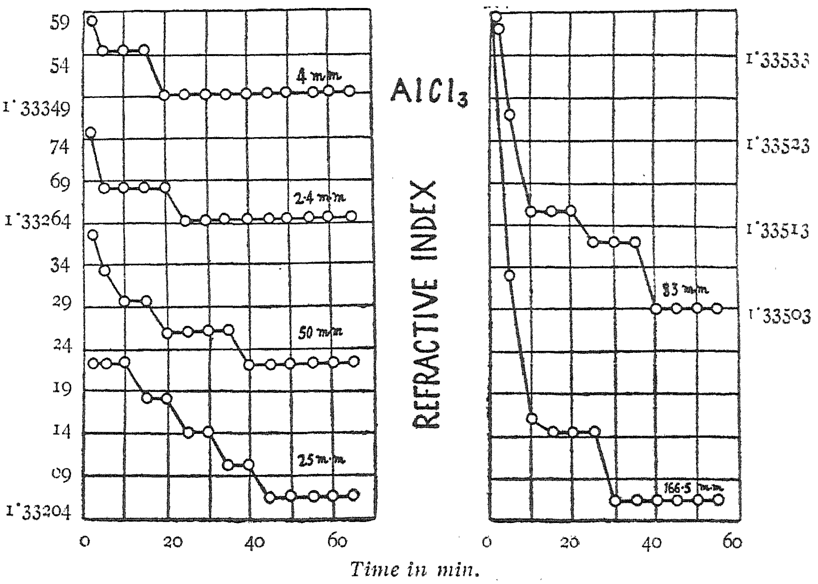
FIG. 3.



the curve shows a break at about 33°. This would appear to be associated partly with some change in the constitution of the dispersion medium, *viz.*, water, since a similar discontinuity has been observed by Osborn (*Phys. Rev.*, 1912, **35**, 216) in the μ-temperature curve for pure water.

Curves of Figs. 1—5 show that variations in μ, attendant on the various types of coagulations, are quite appreciable and irregular. The latter feature is found to be marked especially in the case of univalent coagulations. A number of experiments was made to see if this apparant irregularity was due to any experimental error. At high concentrations, that is, in moderately rapid coagulations, the results were both more uniform and satisfactorily reproducible. In very slow coagulations the reproducibility was found to be less. This, however, could not be traced to any deficiency in the accuracy and the sensitivity of apparatus. Moreover, this was observed generally towards the final stages of the coagulation. Some of the results obtained in this connection are interesting. Comparing for example curves 1 and 2 in Fig. 1 due to the least and the largest concentration of the electrolyte, it is seen that the former shows more fluctuations. It was possible to reproduce all points in curve 2 in Fig. 1 corresponding to rapid coagulation. When the experiment corresponding to curve 1 shown by triangles was repeated a number of times, in the majority of cases all the points shown on the curve 1, Fig. 1 were obtained; the two points which were sometimes missed were at α and β, in the minimum; they, however, appeared during the coagulation at positions shown by the dotted triangles. A similar effect was observed in curve 3, Fig. 1 shown by continuous squares corresponding to 25 millimols of KCl; points γ and δ appeared at positions shown by corresponding dotted squares in some of the repetitions of the experiments. Similar results were obtained in the reproductions of other results which have not been shown for want of space, and whose common indication was that points generally towards the close of the coagulation did not appear at the same time, and then, a whole fluctuation was missed, so that the final section showing a constancy of refractive index appeared earlier. On comparing these curves in Fig. 1 for the slowest coagulations with curves in Figs. 2—5, it is seen that the former do not show an *overall* change in the refractive index consequent upon coagulation. Precisely similar results were obtained earlier (Joshi and Viswanath, *loc. cit.*) where it was found that while moderately rapid coagulations of colloid arsenious sulphide yielded uniform and progressively rising viscosity-time curves, *slow* coagulations corresponded markedly to discontinuous changes without a *net* rise of viscosity produced during the period observed. This has been confirmed by subsequent results in the case of numerous other coagulations (Joshi and coworkers, *loc. cit.*).

FIG. 4.



In view of the sensitivity of μ to temperature changes, it is important to see that these latter are not responsible for the observed fluctuations on the μ—time curves. From the data obtained for the influence of temperature on μ (*cf.* Fig. 6), it is seen for example that the discontinuities on the various μ—time curves in Fig. 1 correspond to temperature changes in the range 1—6°. This is definitely inadmissible, since the temperature of the coagulating system was certainly constant within 0·1 to 0·05°. The possibility of the accumulation coagulum on the face of the prism in the refractometer was also examined. In the first instance, the mixture was well stirred throughout the progress of the coagulation and secondly with a given colloid a deposition of its precipitate would alter μ in the same sense in all coagulations irrespective of the nature of the coagulant, which is contrary to facts as observed here. While results in Fig. 2, obtained with other monovalent coagulants, are substantially similar to those discussed already in the case of KCl in Fig. 1, it is interesting to see from Fig. 3 that the influence of the trivalent lanthanum and bivalent strontium salts is to raise μ during coagulation. Results with barium chloride were clearly analogous.

The specificity of the influence of the coagulant on μ change is further brought out by curves in Figs. 4 and 5, where in coagulations by thorium nitrate and aluminium chloride, μ is seen to change in a sense opposite to that observed previously in Fig. 3. One rather suggestive and general result from curves in Figs. 1-5 is that the progress of coagulation as recorded by μ-change is markedly discontinuous, and that this feature is more pronounced the *slower* the coagulation, especially with univalent coagulants. The concentration of the coagulator would appear to determine both the number and duration of each of these *zones of coagulation*, during any one of which μ remains constant and changes abruptly to a new value which in its turn prevails for a time, and so on. In earlier papers in this series (*loc. cit.*) on the deficiency in the application of Smoluchowski's theory of the kinetics of coagulation (*loc. cit.*) the view was emphasized on experimental grounds that contrary to Smoluchowski's fundamental assumption, coagulation was more complex than a mere continued aggregation of primary particles, and also that the process was not *time continuous*, especially in the '*slow*' region. The results in Figs. 1—5 support this view, and also serve to indicate the utility of refractivity measurements as a systematic and sensitive means of exploring the course of coagulation.

FIG. 5.

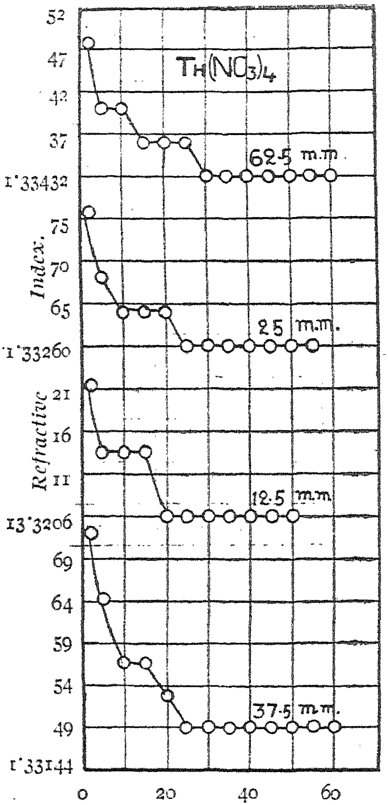
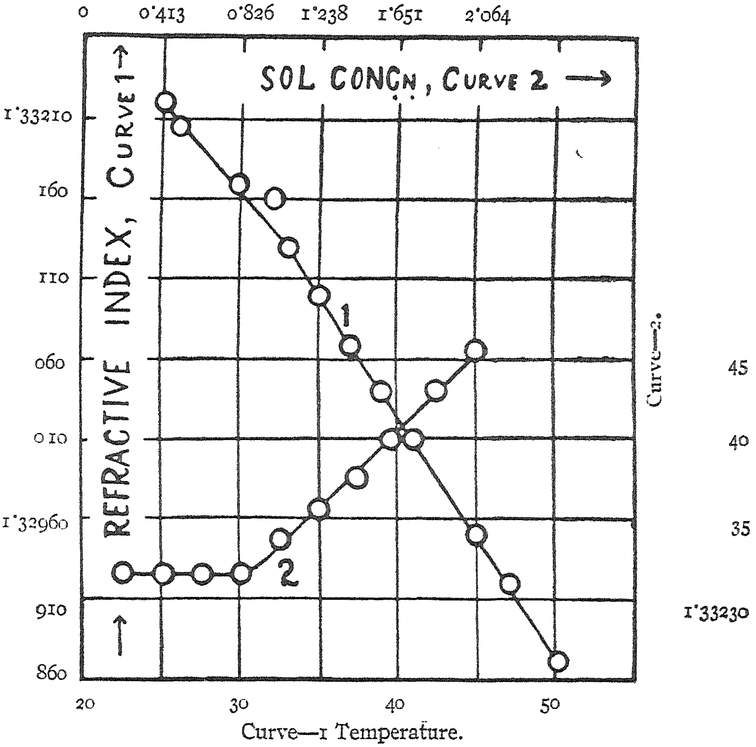


FIG. 6.



SUMMARY.

1. Progress of coagulations of colloid manganese dioxide by different concentrated solutions of HCl, Li_2SO_4, NaCl, KCl, NH_4Cl, $SrCl_2$, $La(NO_3)_3$ and $Th(NO_3)_4$ has been followed by measurement of μ, the refractive index with a Pulfrich refractometer.

2. The nature of the μ—time curve depends upon the nature and the concentration of the coagulant.

3. These curves have been found to be discontinuous in all the cases examined. It is postulated that coagulation is not time continuous, but occurs through successive and discontinuous stages called "*Zones of coagulation*" which tend to become conspicuous in the *slow* region.

4. μ-and the colloid content, and μ-and temperature were found to be related linearly, except for very small concentrations of the sol, and also at lower temperatures.

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Application of the Thiocyanogen Value in the Quantitative Determination of Oleic and Linolic Acids in Natural Oils, which are free from Linolenic Acid, according to Kaufmann.

By S. K. Sharma

There appears to be a considerable confusion in the scientific literature regarding the application of Kaufmann's method for calculating the respective percentages of the various unsaturated acids or their glycerides in natural oils on the basis of thiocyanogen value. Kaufmann (*Analyst*, 1926, **51**, 157, 264) has shown that linolic acid or glyceride combines with thiocyanogen only at one of the two double bonds, so that a knowledge of the thiocyanogen value (generally calculated in terms of iodine) and of the iodine value of an oil makes possible the calculation of the linolic and the oleic glyceride content of an oil as shown below:

Theoretical values

Iodine value of oleic acid = 89·93	Thiocyanogen value of oleic acid = 89·93
,, ,, linolic acid = 181·14	,, ,, linolic acid = 90·57

Let O and L be the respective percentages of oleic and linolic acids in an oil. Then we can have

1. $0·899 \times O + 1·812 \times L = \text{Iodine value}$
2. $0·899 \times O + 0·906 \times L = \text{Thiocyanogen value}$

From 1 and 2 we have

$$\text{I}\quad \begin{cases} L = 1·104\ (\text{Iodine value—Thiocyanogen value}) \\ O = 1·112\ (2\ \text{Thiocyanogen value—Iodine value}) \end{cases}$$

From these we can find the percentage of the corresponding glycerides in the oil by the following equations :

$$\text{II}\quad \begin{cases} \text{Linolic glyceride} = 1·154\ (\text{Iodine value} - \text{Thiocyanogen value}) \\ \text{Oleic glyceride} = 1·162\ (2\ \text{Thiocyanogen value} - \text{Iodine value}) \\ \text{Saturated glyceride} = 100 - 1·158 \times \text{Thiocyanogen value} \end{cases}$$

If a particular oil contains more than 1% of unsaponifiable matter, then the total fatty acids are set free after previous removal of the unsaponifiable matter and their iodine and thiocyanogen values determined. The proportion of linolic, oleic and saturated acids in the mixed fatty acids is calculated by the following equations:

$$\text{III}\quad \begin{cases} \text{Linolic acid} = 1·104\ (\text{Iodine value} - \text{Thiocyanogen value}) \\ \text{Oleic acid} = 1·112\ (2\ \text{Thiocyanogen value} - \text{Iodine value}) \\ \text{Saturated acid} = 100 - 1·108 \times \text{Thiocyanogen value} \end{cases}$$

In continuation of Paul Arup's work on Irish butter (*Analyst*, 1932, **57**, 610) Budhalakoti and Mukherji (*J. Indian Chem. Soc.*, 1935, **12**, 455) have correctly calculated the linolic acid content of Indian butter fats by multiplying the difference of iodine and thiocyanogen values (of course determined with the butter) by 1·104. But they have given the equation

$$S+O+L=100$$

which is inadmissible in so far as the butter, whose values they have determined, or in fact every oil or fat contains besides the fatty acids a considerable amount of glycerol. The total of fatty acids, therefore, cannot be equated to 100. This equation, however, does not enter into the calculation.

Firstly, Godbole and Sadgopal (*Allgem. Fett. Ztg.*, 1934, 435) have determined the thiocyanogen values of several Indian oils and have calculated the percentages of oleic and linolic acids by using the equations II which are really meant for the calculation of glycerides as has been shown above. Therefore, the columns, in which the values of oleic and linolic acids are shown, really indicate the percentage of the corresponding glycerides in the oil. The given percentages of fluid acids, in fact, represent the percentages of unsaturated glycerides; and the percentages of solid acids, the percentages of saturated glycerides. The percentage of saturated or solid acids in an oil, as a rule, cannot be calculated correctly on the basis of its iodine and thiocyanogen values without knowing the composition of such acids.

Secondly, apart from the application of the wrong equation there is throughout an inexplicable error in the author's calculation (*cf.* column nos. 5 and 6 with nos. 13 and 14 of the table on the next page).

Thirdly, the olive, *mahua*, and *neem* oils have been reported to contain 1·2, 6·5 and 5·2% of unsaponifiable matter and yet no consideration has been made for that. The iodine and thiocyanogen values of the oil are not applicable in such cases (Wizoff, "Einheitliche-untersuchungs Methoden für oel und Fett Industrie" 1930, II Auflage, p. 95), the unsaponifiable matter of oil here examined having iodine values varying between 64 and 206 according to Bolton and Williams (*Analyst*, 1930, **55**, 1).

Fourthly, the calculation of theoretical iodine values from the calculated oleic and linolic acid content is incorrect. Such theoretical iodine values of the fatty acids, if no consideration is made of the unsaponifiable matter, will always be higher than that of the oil but in the case of cocoanut oil, lard and *neem* oil, they have shown values

	Table by Godbole and Sadgopal.										As corrected by S. K. Sharma.				
					Calculated % of		Calculated % of fatty acids by method of difference		Iodine value of fatty acids		Calculated % of		Calculated % of		
Name of oil.	Unsaponifiable.	Iodine value (Hanus).	Hexabromide.	Thiocyanogen value.	Oleic acid.	Linolic acid.	Fluid.	Solid.	Experimental.	Theoretical.	Oleic acid.	Linolic acid.	Oleic glyceride.	Linolic glyceride.	Saturated glyceride by method of difference.
Almond oil	0	96	0	83·5	78·63	14·02	92·65	7·35	96·6	96·5	78·96	13·8	82·5	14·42	3·08
Apricot oil	0·4	104·2	0	66·75	32·02	41·9	73·92	26·0	109·6	105·2	32·58	41·34	34·05	43·22	22·73
Arachis oil	0·5	97·2	0	74·0	56·15	25·94	82·09	17·9	101·5	98	56·49	25·62	59·03	26·77	14·2
Butter fat (cow)	0·1	40·2	0	35·5	34·47	4·97	39·44	60·5		40·6	34·26	5·19	35·8	5·42	58·78
Butter fat (buffalo)	0·45	41·8	0	37·8	37·9	4·0	41·9	58·1		41·48	37·58	4·42	39·27	4·62	56·11
Castor oil	0·3	85·2	0	87·75											
Chalmoogra oil	0·35	90·1	0	86·5	91·4	4·74	96·14	3·85	86·1	91·0	92·19	3·97	96·44	4·16	—0·60
Cocoanut oil	0·2	10·8	0	10·9	10·34	0·0	12·34	87·7	8·35	10·5	12·23	0·0	12·78	0·0	87·22
Olive oil	1·2	105·2	0	64·9	26·8	45·0	71·8	21·15	110·35	106·2					
Lard	0·2	55·4	0	47·25	43·14	9·32	52·46	47·54	54·4	55·0	43·48	9·0	45·43	9·41	45·16
Mahua oil	6·5	62·5	0	48·6	37·47	16·45	53·92	46·1	66·4	63·5					
Neem oil	5·2	64·2	0	62·6	67·3	2·3	69·6	30.4	62·15	63·94					
Beef tallow	0·54	39·4	0	34·9	33·58	5·18	38·76	61·23	41·35	39·7	33·81	4·97	35·33	5·19	59·48
Mutton tallow	0·6	41·5	0	35·0	82·02	6·85	38·87	61·29	39·0	41·5	31·69	7·17	33·11	7·51	59·38
Cocoanut fat	0·75	34·8	0	34·9	38·14	0·66	38·8	61·2	29·75	35	38·92	0·0	40·67	0·0	59·33

even lower than that of the oil (*vide*, Table column 10). Consequently it is doubtful if the iodine value check, on the basis of their observed iodine and thiocyanogen values, can be used to support the suitability of Kaufmann's thiocyanogen value method for the determination of unsaturated acids in the oils examined by them.

Further Varma, Godbole and Gangadharan (*Fettchem.*, 1935, **5**, 88) determined the iodine and thiocyanogen values of the oil from the seeds of *Sarcostigma Klinii* and applying the equations (I) for the calculation of acids in the oil have quoted the following values which are erroneous

Iodine value = 69·16	Linolic acid = 10·82%
Thiocyanogen value = 49·48	Oleic acid = 55·18 ,,
	Saturated acids = 34·00 ,,

By the same equations (I) the correct values should be

Linolic acid = 21·72% or glyceride = 22·71%

Oleic acid = 33·13% or glyceride = 34·62%

and saturated glyceride = 42·71%

In this paper also the percentage of saturated acids has been obtained by subtracting the sum of unsaturated ones from 100, which is incorrect as indicated above, but what is most striking in this paper is that the authors claim support for this doubly wrong value of saturated acids from the results of Bertram's oxidation method (*Chem. Weekbald.*, 1927, **24**, 226) for which it is claimed that the greatest error found in test experiments was −0·7 % while usually the error was much less (*cf.* Mitchell, "Recent Advances in Analytical Chemistry", 1930, p. 64.)

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New Aspects of Nitrogen Fixation and Conservation in Soil. Part I.

By N. R. Dhar and S. K. Mukerji.

In publications from this laboratory, it has been emphasised that light plays an important rôle in many oxidation processes taking place in the soil and that chemical and not microbial agencies may be active in these reactions (*cf.* Dhar, " Influence of Light on some Biochemical Processes " 1935).

We are carrying on a systematic investigation on different types of nitrogen fixation and in this communication some of our results are recorded. Experiments showing that carbohydrates can conserve soil nitrogen are also recorded in this paper.

Nitrogen Fixation in the Photo-oxidation of Cane sugar mixed with Sterilised Soil in Quartz Vessels.

The cane sugar, the soil and the quartz vessels were sterilised in an autoclave for 2½ hours at 20 lb. pressure. In each experiment 25 c. c. of sterile distilled water were added and the quartz vessels were exposed to sunlight. The mouths of the vessels were covered with plugs of sterile cotton wool.

Method of Analysis.—For estimating the ammoniacal nitrogen present in the soil, 50 g. of the soil which was dried in a steam oven was treated with 5 g. of pure potassium chloride and 5 g. of pure magnesium oxide and 50 c. c. of water and distilled for 6 hours on a water-bath and at the same time a rapid current of air, purified by passing through a solution of ferrous sulphate and sulphuric acid, was aspirated. The ammonia was absorbed in two flasks containing standard solutions of sulphuric acid.

For the estimation of nitric nitrogen, the soil from which ammonia was removed by the previous procedure, was treated with one gram of

Devarda's alloy free from ammonia and nitrate and 25 c. c. of 1% sodium hydroxide solution and left overnight for the reduction of nitrite and nitrate to ammonia. When the reduction was complete, the ammonia set free was determined as in the first stage colorimetrically by Nessler's reagent.

The total nitrogen was estimated according to the method of Robinson, McLean and Williams (*J. Agric. Sci.*, 1929, **19**, 315) by heating 5 g. of well dried and powdered soil with 20 c. c. conc. sulphuric acid, 5 g. fused potassium sulphate and a few crystals of copper sulphate for 4 hours. The ammonium sulphate thus formed was estimated as before. In this method the total carbon is also determined simultaneously by absorbing the sulphur dioxide produced in a standard iodine solution, the excess of which is titrated against a standard thiosulphate solution. The sum of the ammoniacal and nitric nitrogen is known as available nitrogen and the nitrogen obtained according to the modified Kjeldahl's method is the total combined nitrogen. The following results have been obtained.

TABLE I.

Exposed to sunlight in February and March, 1935.

	NH_3—N.	Nitric-N.	Available N.	Total N.	Total C.
Original soil	0·000734%	0·0035%	0·004234%	0·0458%	0·5055%
100 G. soil + 1 g. cane sugar + 50 c. c. water exposed for 145 hours in 250 c. c. quartz flask.	0·00116	0·00402	0·00518	0·0466	0·7215
100 G. soil + 2 g. cane sugar + 50 c. c. water exposed for 284 hours in 250 c. c. quartz flask.	0·00155	0·00386	0·00541	0·0486	1·2245
100 G. soil + 4 g. cane sugar + 50 c. c. water exposed for 284 hours in 250 c. c quartz flask.	0·00175	0·00386	0·00561	0·0486	1·7010

TABLE II.

Exposed to sunlight from 30th April to 15th July 1935.
Total exposure for 480 hours.

	NH_3–N.	Nitric-N.	Available N.	Total N.	Total C.
Original soil	0·000902%	0·00368%	0·00458%	0·0474%	0·5349%
50 G. soil + 2 g. cane sugar + 25 c. c. water in 250 c. c. quartz flask.	0·001646	0·00396	0·005606	0·04921	1·686
50 G. soil + 4 g. cane sugar + 25 c. c. water in 250 c. c. quartz flask.	0·00143	0·0035	0·00493	0·0519	3·012
50 G. soil + 1 g. cane sugar + 25 c c. water in a quartz boiling tube.	0·001422	0·0035	0·004922	0·0509	0·871
50 G. soil + 4 g. cane sugar + 25 c. c. water in a quartz boiling tube.	0·001454	0·00364	0·005094	0·054	2·998

The foregoing results show that in all cases when cane sugar and sterile soil are exposed to light in quartz vessels, there is an appreciable increase in the total nitrogen and ammonia contents. It appears, therefore, that the energy set free in the photo-oxidation of sugars can fix atmospheric nitrogen in the soil. The researches of Palit and Dhar (*cf.* Dhar, "New Conceptions in Biochemistry") show that sugars are oxidised by air when exposed to sunlight. Recently Ghosh and Rakshit (*J. Indian Chem. Soc.*, 1935, **12**, 357) have obtained similar results.

Nitrogen Fixation in the Induced and Catalytic Oxidation of Glucose or Cane Sugar.

Air aspirated through two Woulf's bottles, one containing a solution of ferrous sulphate in sulphuric acid and the other concentrated sulphuric acid in order to remove the oxides of nitrogen and ammonia and to kill the bacteria, was passed through an Erlenmeyer flask containing a weighed amount of glucose or cane sugar and ferrous hydroxide obtained from 1 g. of ferrous sulphate and an equivalent amount of caustic potash. After passing air, the amount of ammonia formed was distilled off by adding alkali and heating. The distillate was absorbed in dilute sulphuric acid and the ammonium sulphate estimated colorimetrically by Nessler's reagent. Two Erlenmeyer flasks containing dilute solutions of sulphuric acid were placed next to the flask containing the inductor, the last one for the absorption of ammonia from the atmosphere of the laboratory. The following experimental results have been obtained.

TABLE III.

	Glucose taken.	Glucose oxidised.	Energy set free.	NH_3-N obtained.	Energy utilised.	Efficiency.
(*a*)	1 G.	0·08 g.	300 Cal.	0·000332 g.	0·512 Cal.	1 :586
(*b*)	0·5	0·064	240	0·000270	0·417	1 :575
*(*c*)	0·5	0·079	296	0·000334	0·515	1 :574
	Cane sugar taken.	Cane sugar oxidised.				
(*a*)	1	0·04	158	0·000245	0·378	1 :418
(*b*)	0·5	0·0347	148	0·000241	0·372	1 :398
*(*c*)	0·5	0·0716	283	0·000462	0·713	1 :396

* (with one gram sodium hydrogen phosphate).

The results recorded in the foregoing table show that the induced oxidation of glucose or cane sugar by passing air in the absence of bacteria leads to the formation of ammonia using an 1 % solution of glucose, 4 mg. of nitrogen are fixed per gram of glucose oxidised by induction, whilst 4·68 mg. of nitrogen are fixed per gram of mannite in its bacterial oxidation (*cf.* Waksman "Soil microbiology" 1927, p. 569). Similar results in 4 mg. of nitrogen fixation have been observed in the induced oxidation of one gram of cane sugar as against 5·9 milligrams in the bacterial fixation (Compare, Lohnis and Pillai, *Centrbl. Bakt.*, 1908 II, **20**, 781). It appears, therefore, that the order of the nitrogen fixation caused by the induced oxidation of glucose or cane sugar is practically the same as in the bacterial fixation.

Nitrogen Fixation in the Oxidation of Cane sugar mixed with Soil and Exposed to Sunlight in Dishes.

In these experiments the garden soil was mixed with pure cane sugar and exposed to sunlight in enamelled dishes covered with ordinary glass plates. For the experiments in the dark, the outer surface of the glass plates was covered with a thick coating of Japan black enamel. The following results were obtained.

TABLE IV.

		NH_3–N.	Nitric–N.	Total available N.	Total N.	Total C.
Exposure for 16 hours spread out from 28th August to 7th September 1935.	250 g. soil alone	0·00356%	0·0021%	0·00566%	0·0466%	0·5134%
	250 g. soil + 20 g. cane sugar	0·00396	0·0021	0·00606	0·0466	4·932
	250 g. soil + 20 g. cane sugar + 10 g. Na_3PO_4	0·00436	0·0021	0·00644	0·0466	5·202
	250 g. soil + 20 g. cane sugar + 0·5 g. N as $(NH_4)_2SO_4$	0·04516	0·00318	0·04834	0·1289	5·721
	250 g. soil + 20 g. cane sugar + 0·5 g. N as $(NH_4)_2SO_4$ + 10 g. Na_3PO_4	0·04668	0·00318	0·04986	0·1272	5·610
	250 g. soil + 0·5 g. N as $(NH_4)_2SO_4$	0·03500	0·0070	0·0420	0·1166	0·5133
Exposure for 74 hours from 28th August to 26th September 1935.	250 g. soil + 20 g. cane sugar	0·00520	0·00208	0·00728	0·0482	4·831
	250 g. soil + 20 g. cane sugar + 10 g. Na_3PO_4	0·00538	0·00208	0·00746	0·0482	5·111
	250 g. soil + 20 g cane sugar + 0·5 g. N as $(NH_4)_2SO_4$	0·0450	0·0032	0·0482	0·1198	5·627
	250 g. soil + 20 g. cane sugar + 0·5 g. N as $(NH_4)_2SO_4$ + 10 g. Na_3PO_4	0·040	0·0032	0·0432	0·1152	5·610
	250 g. soil + 0·5 g. N as $(NH_4)_2SO_4$	0·010	0·029	0·039	0·070	0·513

TABLE IV (continued).

		NH_3 – N.	Nitric – N.	Total available N.	Total N.	Total C.
Exposure for 400 hours from 28th August to 18th November, 1935.	250 g. soil + 20 g. cane ugar. s	0·0070	0·00334	0·01034	0·0537	1·532
	250 g. soil + 20 g. cane sugar + 10 g. Na_3PO_4	0·0075	0·00350	0·0110	0·0560	1·411
	250 g. soil + 20 g. canesugar + 0·5 g. N as $(NH_4)_2SO_4$	0·0468	0·0050	0·00518	0·1010	1·872
	250 g. soil + 20 g. cane sugar + 0·5 g. N as $(NH_4)_2SO_4$ + 10 g. Na_3PO_4	0·0483	0·00524	0·05354	0·1152	1·789
	250 g. soil + 0·5 g. N as ammonium sulphate	0·010	0·00280	0·038	0·066	0·513

The above results show that when soil is mixed with cane sugar in presence or absence of sodium phosphate and exposed to sunlight, the ammoniacal, nitric and total nitrogen increase due to the fixation of the atmospheric nitrogen.

In presence of 0·5 g. of ammoniacal nitrogen added as ammonium sulphate to 250 g. soil and 20 g. cane sugar, there is no evidence of nitrogen fixation as the total nitrogen content is 0·101%, whilst the amount actually present should have been 0·1466% (0·1% added as ammonium sulphate and 0·0466% originally present in the soil). It is quite possible that the fixation if any, may have been compensated by the denitrification, which is known to take place under ærobic conditions. Moreover, these experiments show that ammonium sulphate readily undergoes nitrification when mixed with soil and exposed to sunlight in dishes and cane sugar markedly retards this nitrification and also the nitrogen loss observed by exposing ammonium salts to light and air.

Our results recorded in previous papers (*Proc. Acad. Sci. U.P.*, 1934, **4**, 175 ; 1935, **4**, 330; 1935, **5**, 61) show that the ammoniacal nitrogen goes on increasing up to a limiting value with the time of exposure to sunlight when the exposure is continued. After this period, further exposure to light leads to a decrease of the ammonical nitrogen and an increase of nitric nitrogen. But the sum of the nitric and ammoniacal nitrogen is less than that obtained before. This behaviour is due to the loss of nitrogen in the gaseous state caused by the photochemical, catalytic and thermal decomposition of ammonium nitrite formed on the soil surface. This type of denitrification is an important soil process taking place when nitrogenous compounds are present in the soil, which is exposed to light and air. A very important conclusion can be drawn from the experiments published in the foregoing papers, that the amount of ammoniacal nitrogen is always greater in the soil mixed with the energy-rich compounds and receiving sunlight than in those kept in the dark (that is, in blackened vessels).

Fixation of Nitrogen in the Oxidation of Molasses mixed with Soil.

Experiments carried on in dishes.—As molasses contain 30-40% cane sugar and 30% invert sugars, it was felt that the oxidation of this substance in the soil would be an excellent source for obtaining the energy required in nitrogen fixation.

Mixtures of molasses and unsterilised soil and small amount of water were exposed to sunlight during the months of March, to November, 1935, and the carbon, total nitrogen, ammoniacal nitrogen and nitric nitrogen were estimated from time to time. In the following tables corrections were applied for the amount of ammonia introduced with molasses, which contained 0·001% ammoniacal nitrogen but no nitric nitrogen. The following results were obtained.

TABLE V.

	Molasses added per kg. of soil.	NH_3-N.	Nitric N.	Available N.	Total N.	Total C.
Exposed for 161 hours.	0 (original soil)	0·000734%	0·0035%	0·004234%	0·0362%	0·4025%
	5 g.	0·000944	0·0040	0·004944	0·0360	0·4521
	10	0·00096	0·0038	0·00476	0·0360	0·5732
	20	0·00106	0·0038	0·00486	0·0360	0·8212
	40	0·00113	0·0038	0·00493	0·0360	1·0640
	75	0·00220	0·0038	0·00600	0·0380	1·5220
	100	0·00222	0·0038	0·00602	0·0460	2·0810
	150	0·00216	0·0038	0·00596	0·0490	3·8840
	190	0·00210	0·0038	0·00590	0·0520	4·4290
Corres-pondnig dark.	10	0·00111	0·00338	0·00448	0·0362	0·5632
	20	0·00097	0·00376	0·00475	0·0362	0·9287
	40	0·00043	0·00376	0·00410	0·0362	1·2310
Exposed for 279 hours.	5 g.	0·00136	0·00412	0·00548	0·0360	0·459
	10	0·00148	0·00412	0·00560	0·0360	0·576
	20	0·00159	0·00412	0·00571	0·0360	0·823
	40	0·00184	0·00412	0·00597	0·0362	1·065
	75	0·00220	0·00400	0·00620	0·0382	1·329
	100	0·00200	0·00324	0·00524	0·0460	1·986
	150	0·00104	0·00284	0·00388	0·0492	3·424
	190	0·00037	0·00224	0·00261	0·0521	4·021

TABLE V (continued).

Corresponding dark.	10 g.	0·00074%	0·00324%	0·00398%	0·0361%	0·552%
	20	0·00051	0·00310	0·00361	0·0361	0·902
	40	0·00041	0·00282	0·00323	0·0361	1·102
Exposed for 850 hours.	5	0·00092	0·00456	0·00548	0·0381	0·412
	10	0·00096	0·00462	0·00558	0·0381	0·542
	20	0·00116	0·00462	0·00578	0·0382	0·671
	40	0·00310	0·00420	0·00720	0·0389	0·912
	75	0·00175	0·00380	0·00555	0·0391	1·213
	100	0·00146	0·00362	0·00508	0·0472	1·321
	150	0·00133	0·00304	0·00437	0·0468	2·321
	190	0·00120	0·00280	0·00400	0·0480	3·280
Corresponding dark.	10	0·00084	0·00320	0·00404	0·0372	0·513
	20	0·00089	0·00316	0·00405	0·0372	0·882
	40	0·00094	0·00316	0·00409	0·0380	1·087
Exposed for 1450 hours.	5	0·00092	0·00452	0·00544	0·0410	0·4125
	10	0·00098	0·00464	0·00562	0·0418	0·4424
	20	0·00118	0·00504	0·00622	0·0433	0·5516
	40	0·00155	0·00490	0·00645	0·0498	0·5827
	75	0·00185	0·00464	0·00649	0·0510	0·6619
	100	0·00162	0·00422	0·00584	0·0525	0·8629
	150	0·00144	0·00396	0·00540	0·0544	1·252
	190	0·00138	0·00324	0·00462	0·0544	2·441
Corresponding dark.	10	0·00084	0·00344	0·00428	0·0380	0·500
	20	0·00090	0·00336	0·00426	0·0380	0·815
	40	0·00096	0·00344	0·00440	0·0380	0·981

The results recorded in the foregoing table show that in all cases when molasses is added to the soil, which is properly aerated, there is an appreciable increase in its ammonia and total nitrogen contents. In these cases also, like those with cane sugar, there is greater increase of ammonia in the vessels exposed to sunlight than in those kept in the dark. The amount of ammonia formed goes on increasing up to a limiting value with increase of exposure. In all these experiments the total carbon goes on decreasing with time.

Field experiments on the alppication of molasses to soil.—In these experiments, known weights of molasses were added to a definite area of the soil in the field. In some experiments, the soils were dug once a week, whilst in others the soil was kept unstirred in order to investigate the influence of aeration. The following results were obtained·

TABLE VI.

	NH_3-N.	Nitric N.	Available N.	Total. N.	Total C.	Date of analysis.
3600 Kg. of molasses added per acre of land on 30-7·35.						
Original soil.	0·00374%	0·00334%	0·00708%	0·0466%	0·542%	30- 7-35
	0·00618	0·00320	0·00938	0·0467	0·673	24- 8-35
	0·00670	0·00350	0·01020	0·0467	0·651	3- 9-35
	0·00554	0·00445	0·00999	0·0467	0·653	21- 9-35
	0·00590	0·00500	0·01090	0·0485	0·543	14-10-35
	0·00468	0·00608	0·01076	0·0482	0·543	6-11-35
	0·00464	0·00608	0·01072	0·0488	0·544	17-12-35
	0·00480	0·00598	0·01078	0·0482	0·548	15- 1-36
7200 Kg. of molasses per acre added on 30-7-35.						
Original soil.	0·00350	0·00280	0·00630	0·0462	0·515	30- 7-55
	0·00508	0·00262	0·00770	0·0467	0·720	24- 8-35
	0·00724	0·00282	0·00906	0·0467	0·714	3- 9-35
	0·00768	0·00382	0·01150	0·0467	0·711	21- 9-35
	0·00734	0·00400	0·01134	0·0492	0·543	14-10-35
	0·00500	0·00668	0·01168	0·0518	0·543	6-11-35
	0·00488	0·00700	0·01188	0·0520	0·544	17-12-35
	0·00480	0·00782	0·01262	0·0522	0·548	15- 1-36
10800 Kg. of molasses per acre added on 5-8-35.						
Original soil	0·00560%	0·00372%	0·00932	0·0522%	0·581	5- 8-35
	0·00612	0·00344	0·00956	0·0579	1·366	24- 8-35
	0·00776	0·00370	0·01146	0·0582	1·238	3- 9-35
	0·01094	0·00358	0·01452	0·0583	1·131	21 -9-35
	0·01028	0·00362	0·01390	0·0588	1·086	14-10-35
	0·00822	0·00576	0·01398	0·0611	0·985	6-11-35
	0·0070	0·0124	0·0194	0·0622	0·821	17-12-35
	0·0056	0·0132	0·0188	0·0624	0·812	15- 1-36

In these field experiments, there is also definite evidence of nitrogen fixation in the soil on the addition of molasses, as there is increase in the available and total nitrogen.

Molasses added to soil in heaps-composts with molasses.—A heap of soil weighing 167 kg. was mixed with 12 kg. of molasses (A) and another heap weighing 174 kg. was treated with 6 kg. of molasses (B) and exposed to air and light. For better aeration, the heaps were stirred frequently after addition of water. The molasses was added on 18th February, 1935 and exposed to sun till the end of June and then removed to a verandah of the laboratory before the rains set in. The following results were obtained.

TABLE VII.

	NH_3-N.	Nitric-N.	Total available N.	Total N.	Total C.
Original soil	0·00865%	0·00582%	0·01447%	0·0458	0·5055
Heap (A) analysed 18·3-35	0·01646	0·00594	0·0224	0·0538	1·9922
Heap (B) ,, ,,	0·00934	0·00594	0·01528	0·0504	1·2380
Heap (A) analysed on 18·4 35	0·0140	0·0058	0·0198	0·0540	..
Heap (B) ,, ,, ,,	0·0116	0·0058	0·0174	0·0512	—
Heap (A) analysed on 20·9-35	0·0175	0·00822	0·02572	0·09005	1·0514
Heap (B) ,, ,, ,,	0·0140	0·00736	0·02136	0·09	1·035

The above results show that when molasses is added to soil in heaps and exposed to air and light, the available and the total nitrogen are considerably increased The total nitrogen is double that of the original amount present in the soil before the addition of molasses. Hence considerable fixation of nitrogen takes place and excellent composts are prepared with molassed soils, of which the carbon-nitrogen ratio becomes normal and attains the value 11·5.

Residual Effect of Molasses added to Fields.

The following results show that molasses when added to the soil in fields produces residual effects.

TABLE VIII.

	Plot A	Plot B	Plot C
	1800 G. of molasses per acre added on 25-9-34 and then wheat grown. Molassed again at the rate of 3600 g. per acre on 30-4-35 and analysed on 6-5-35.	Original unmolassed but wheat grown. Molassed at the rate of 3600 kg. per acre on 30-4-35 and analysed on 6-5-35.	Control unmolassed, wheat grown, analysed on 6-5-35.
NH_3N	0·006%	0·0058%	0·0051%
Nitric N	0·0037%	0·0032	0·0029
Total N	0·0321%	0·0272	0·0224
Total C	0·5428%	0·5321	0·2621

The foregoing results show that Plot A, which has been molassed twice, contains more available and total nitrogen than Plot B, which has been molassed once and Plot C, which has not been molassed at all.

The foregoing results obtained with molasses, when mixed with soil, show that there is an appreciable increase in the total nitrogen and ammonia contents ; the amount of ammonia goes on increasing up to a limiting value, when it decreases. But at this stage the nitrate content increases appreciably due to the oxidation of the ammonium salts formed by nitrogen fixation. When the amounts of molasses added to the soil are not large, the maximum amount of ammonia to be formed due to nitrogen fixation in the soil is reached within two months. After this stage the nitrate increases due to oxidation of the ammonium salts produced from the nitrogen fixation in the soil and there is loss of the total available nitrogen and the carbon-nitrogen ratio approaches the 11 : 1 value. Hence, it is concluded that at the stage when the nitrate content of the soil begins to increase appreciably, the soil is most suitable for the sowing of crops. When larger quantities of molasses are added to the soil in the fields, more time is required to attain the stage of nitrate increase. For example, from the results recorded in Table VI, it will be seen that in the plot in which 270 maunds of molasses per acre were added, the largest amount of ammonia was fixed but the time required in reaching the maximum was about 3 months. Similarly in the experiments with molasses and soil kept in dishes, the maximum increase of ammonia is attained after a longer exposure to sunlight in those dishes containing larger amounts of molasses than those with smaller amounts Thus with 10 grams of molasses when added to a kilogram of soil the maximum amount of ammonia formation is reached after 279 hours of exposure to sun light spread over 75 days, whilst with 40 grams, the maximum is reached after 850 hours of exposure spread over 4 months. It is clear, therefore, that if the cultivator can afford to wait and can use large amounts of molasses better results are expected than with smaller amounts. Using 270 maunds of molasses per acre of land and if digging or turning over of the soil is continued for about 3 months, once in 10 days, excellent results are expected. With smaller amounts varying from 90 to 180 maunds of molasses per acre, an interval of 8 to 12 weeks with occasional digging ought to be sufficient, because the maximum ammonia formation in these cases is within the above interval. It is well known that the amount of nitrogen fixation in a bacterial culture of Azotobacter is quantitively measured by the ammonia formed. Hence, the evidence of nitrogen fixation in our experiments when molasses of cane sugar is added to the soil is quite definite, because there is not only considerable increase of ammoniacal nitrogen but simultaneously the total nitrogen is also increased. Moreover, in a recent communication, we have shown that in soils, the available nitrogen increases with the increase in total nitrogen.

Our experimental results show that when the soil is not properly aerated after the addition of molasses, the acidity increases and the nitrogen fixation is less.

Many people have tried to use molasses in increasing soil fertility but uniformly good results could not be obtained as will be evident from the following lines:—

" Increased yields of sugarcane have followed the application of molasses to soils at the Station Agronomique and on Mr. Ebbels' estate in Mauritius, where the residual effect is well shown, and also in Antigua. Peck in Hawaii, on the other hand, observed marked losses of nitrate, as also did Harrison in British Guiana."

" Laboratory investigations in humid climates suffer from the difficulty that the soils already contain so much nitrogen that small changes are difficult to measure accurately, and there are losses of nitrogen which counterbalance any fixation. Investigation would be easier in some of the soils very poor in nitrogen found in hot, arid conditions. Rigid incontestable proof could be furnished only by a demonstrated gain in nitrogen effected by Azotobacter, all other possibilities being ruled out. This proof has not yet been forthcoming " (Russell " Soil Conditions and Plant Growth," 1932 pp. 342-44).

" In view of the fact that the energy added to the soil is not directly available to the nitrogen-fixing bacteria and that small amounts of available nitrogen are always present in the soil, and the error in the laboratory determination of total nitrogen by the Kjeldahl method is greater than the possible amount of nitrogen fixed by non-symbiotic bacteria, we are still unable to decide the question definitely." (Waksman, " Soil Microbiology " 1927, p. 587).

" Wide use is being made in systems of agriculture of the bacteria, which work with legumes, but the nitrogen fixing power of those which work outside the plant is as yet not utilised extensively by man, since the methods of controlling them are not well understood "

(Miller:, "The Soil and its Management" 1924, p. 203). A. Koch, J. Litzendorff, F. Krull, and A. Alves (*J. Landw.*, 1907, **55**, 355) have reported nitrogen fixation in plates and pots with dextrose but Pfeiffer and Blanck (*Landw. Versuchs—Stat.*, 1912, **78**, 375) could not obtain any nitrogen fixation with sugar. According to Hutchinson (*J. Agric. Sci.*, 1918, **9**, 92) sugars show beneficial results in autumn but not in spring.

Dr. H. W. Kerr has reported the following yield of sugarcane on applying 10 tons of molasses per acre in the Bundaberg farm in Queensland.

Without molasses	22·7 tons per acre.
10 tons molasses	37·1 tons per acre.

On the other hand, Crabtree working in the Fairy Mead farm in Queensland did not find any beneficial effect with molasses (Proc. Second Annual Conference of Queensland Society of Sugar-cane Technologists, 1932). On applying molasses to the growing crop, no beneficial effect was obtained at Pusa. Recently, an increase of yield to the extent of 36% has been reported at the Shahjahanpur Government Farm on applying 270 maunds of molasses per acre in the cultivation of sugarcane, before planting. Messrs Parry & Co. Ltd., of Madras has also obtained an increase of 40% in the yield of sugarcane. But when molasses was added to the growing crop, no beneficial result was obtained. It will thus be evident from the foregoing observations that up till now the conditions for obtaining uniformly good results from molasses as a manure and the mechanism of the process have not been worked out. In this as well as in previous publications (Dhar and Mukerji, *Proc. Acad. Sci. U.P.*, 1934, **4**, 175; 1935, **4**, 330; 1935, **5**, 61) we have established that the oxidation of the carbohydrates present in molasses either through the agency of bacteria or sunlight or induction and the intermediate products to carbondioxide and water liberates energy in the soil and this energy is utilised in the fixation of atmospheric nitrogen and that is why the ammonia and the total nitrogen contents increase and thus beneficial results in the growth of crops are obtained with molasses as fertiliser. Moreover, as molasses, contain lime, potash and phosphates, its fertilising value is also increased by the presence of these substances. It is interesting to note here that previous workers determined only the total nitrogen of the soil after the addition of energy-rich compounds, and as the difference in total nitrogen is not very high before and after the addition of energy-rich compounds to the soil, they were doubtful regarding the fixation of nitrogen in the soil by the addition of energy-rich compounds. But as we have estimated, both the available (ammoniacal and nitric nitrogen) and the total nitrogen, we have been able to detect the increase of available nitrogen and also total nitrogen in all cases when energy-rich organic compounds are added to well-aerated soils.

It has already been stated that many workers have failed to obtain beneficial results with molasses. Our experiments show that the failure is due to insufficiency of oxidation of the carbohydrates caused by the lack of the aeration of the soil. When the aeration of the soil is insufficient, the increase of ammonia is less and the soil becomes acidic. The amount of fixation of nitrogen depends on the energy available from the oxidation of the carbohydrates of molasses and the bye-products formed from the partial oxidation of carbohydrates and that is why sufficient oxygen is necessary for obtaining beneficial results, and this is achieved if the soil is dug or turned over once a week or 10 days during the period of eight to twelve weeks between the application of molasses to the field and the sowing of crops.

In cold countries, the soil temperature being low and due to lack of sunshine, the velocity of the oxidation of energy-rich substances present in the molasses is small and thus the energy available from the oxidation of carbohydrates may be too small for any marked nitrogen fixation. That is why, many workers like Pfeiffer and Blanck, Hutchinson and others were unable to find beneficial effects with sugars. Moreover, in temperate climates, Azotobacter is not suitable for nitrogen fixation, as the fixation at 10° and lower temperatures is practically nothing. The soil temperature in colder countries being lower than 10° most of the time in the year, practically no nitrogen fixation by Azotobacter is possible and that is why Azotobacter has not been utilised by agriculturists in cold countries. Thiele (*Landw. Versuchs-Stat.*, 1905, **63**, 161) measured the soil temperatures of arable and grass lands daily for three years at Breslau, Germany and reported that only rarely were they favourable for Azotobacter. In tropical countries, however, if the soil is well ploughed after the addition of molasses, there is no reason why soil fertility regarding combined nitrogen should not be increased. We have applied molasses to more than 30 plots of land in different portions of the University compound and in several fields in Cawnpore and we have always observed marked increase in the ammonia and total nitrogen contents of the soils on the application of molasses. In most of our field experiments the amount of ammonia after the addition of molasses and aeration has become three times the amount originally present in the soil. Also Azotobacter requires more heat than Bacillus radicicola and several other bacteria and is eminently suitable for nitrogen fixation in tropical countries except in the months of May and June when the soil temperature in the day time exceeds 50°, beyond which Azotobacter is unable to fix nitrogen. This bacteria should be widely utilised in the fixation of nitrogen in tropical countries when fed with energy-rich substances like molasses, press cakes, etc.

Molasses in the Conservation of Soil Nitrogen.

Apart from the fixation of nitrogen, molasses act as a protector of soil nitrogen and appears to be more effective as a soil fertilizer than ammonium sulphate alone, specially in tropical countries. Our experiments recorded in Tables XI, XII and XIII, show that the loss of nitrogen from the soil on adding ammonium sulphate is decreased when along with ammonium sulphate molasses is added. We have shown that when ammonium sulphate is added to soil in shallow enamelled dishes and exposed to sunlight in the months of May, June and July at Allahabad, as much as 60% of the ammonium salt is lost. This loss can be minimised by adding molasses along with ammonium sulphate. It appears, therefore, that the value of ammonium sulphate or urea as a manure to be used in tropical countries is likely to be greatly enhanced if it is mixed with molasses or any other carbonaceous material. From the foregoing lines, it will be clear why farmyard manure or green manure produces better results in crop yields than ammonium sulphate, because the carbonaceous substances present in the farmyard or green manure, markedly retards the velocity of the oxidation of the nitrogenous compounds present in the farmyard and green manures and retard the processes of ammonification and nitrification and act as an agent in conservation of the nitrogen added. Oil cakes containing fats and nitrogenous substances ought to be effective as a nitrogenous manure in tropical countries, because fats are known to retard the oxidation of nitrogenous compounds.

Russell ("Soil Conditions and Plant Growth," 1932, pp. 76-78 and 313-361) has reported that the yield of barley and straw with farmyard manure in the Rothamsted field experiments from 1852-1922 is better than that obtained with complete artificial manures containing ammonium salts, potassium salts and phosphates. This is due to the fact that there is more nitrogen in the field manured with cowdung than with artificials as is evident from the following data from the Rothamsted fields:—

TABLE IX.

	Total N.
(1) Receiving no manure since 1843	0·095%
(2) Receiving farmyard manure since 1852	0·256
(3) Receiving complete artificials $(NH_4)_2SO_4$	0·099
(4) Receiving complete farmyard manure	0·253
(5) Receiving potash & phosphate but no nitrogen	0·090

TABLE X.

Total nitrogen balance-sheet (1865-1914) *in the top nine inches of soil.*

	Farmyard manure.	Without manure.	Complete Plot 7	artificials. Plot 13
Total N in soil in 1865 lb/acre.	4850	2960	3390	3320
,, ,, ,, per cent.	0·196	0·114	0·123	0·121
,, ,, in 1914 lb/acre.	5590	2570	3210	3240
,, ,, ,, per cent.	0·236	0·092	0·120	0·122
Total change in 4 years lb/acre.	+740	−390	−180	−80

In order to investigate the retarding influence of molasses on the loss of nitrogen from soils, the following field experiments were performed. 270 G., 540 g. and 1080 g. of ammonium sulphate dissolved in water were applied to three plots on 26th September, 1935, the area of each plot being 144 sq. ft. To three other plots, the same amounts of ammonium sulphate were added along with 12 kilograms of molasses (*i.e.*, at the rate of 3600 kilograms per acre). All these plots were ploughed before the application of the ammonium sulphate and were dug once in 10 days afterwards. From time to time, the ammoniacal nitric and total nitrogen and total carbon were estimated. The following results were obtained.

TABLE XI.

270 G. of $(NH_4)_2SO_4$ per 144 sq. ft. of land used.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Unmolassed	0·00832%	0·00350%	0·01182%	0·0583%	0·416%	27-9-35
Molassed	0·00814	0·00350	0·01164	0·0588	0·587	,,
Unmolassed	0·00636	0·00556	0·01192	0·0583	0·416	12-10-35
Molassed	0·00778	0·00426	0·01204	0·0609	0·578	,,
Unmolassed	0·00608	0·00600	0·01208	0·0538	0·416	24-10-35
Molassed	0·00778	0·00582	0·01360	0·0625	0·501	,,
Unmolassed	0·00438	0·00714	0·01152	0·0538	0·411	7-11-35
Molassed	0·00700	0·00636	0·01336	0·0636	0·498	,,
Unmolassed	0·00420	0·00714	0·01130	0·0538	0·412	13-12-35
Molassed	0·0064	0·0064	0·0128	0·0634	0·500	,,

TABLE XII.

540 G. of $(NH_4)_2SO_4$ per 144 sq. ft. of land used.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Unmolassed	0·01206%	0·00344%	0·01550%	0·0603%	0·417%	27-9-35
Molassed	0·01228	0·00344	0·01572	0·0608	0·587	,,
Unmolassed	0·00768	0·00636	0·01404	0·0609	0·416	12-10-35
Molassed	0·01076	0·00436	0·01512	0·0636	0·573	,,
Unmolassed	0·00754	0·00636	0·01390	0·0593	0·421	24-10-35
Molassed	0·01000	0·00636	0·01636	0·0673	0·507	,,
Unmolassed	0·00538	0·00776	0·01314	0·0583	0·418	7-11-35
Molassed	0·00896	0·00874	0·01770	0·0667	0·502	,,
Unmolassed	0·00502	0·0078	0·01282	0·0583	0·418	13-12-35
Molassed	0·00880	0·0088	0·0176	0·0667	0·500	,,
Unmolassed	0·00488	0·0080	0·01288	0·0574	0·422	10-1-36
Molassed	0·0080	0·0080	0·016	0·067	0·512	,,

TABLE XIII.

1080 G. of $(NH_4)_2SO_4$ per 144 sq. ft. of land used.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C	Date of analysis.
Unmolassed	0·02032%	0·00356%	0·02388%	0·0757%	0·416%	27-9-35
Molassed	0·02044	0·00384	0·02428	0·0757	0·585	,,
Unmolassed	0·00874	0·00932	0·01806	0·0700	0·416	12-10-35
Molassed	0·0140	0·00636	0·02036	0·0760	0·574	,,
Unmolassed	0·00754	0·01040	0·01794	0·0636	0·416	24-10-35
Molassed	0·01272	0·00874	0·02146	0·0823	0·574	,,
Unmolassed	0·00636	0·01166	0·01802	0·0612	0·422	7-11-35
Molassed	0·01000	0·00972	0·01972	0·0828	0·552	,,
Unmolassed	0·00578	0·0116	0·01738	0·0610	0·422	13-12-35
Molassed	0·0096	0·0098	0·0194	0·0830	0·542	,,
Unmolassed	0·0056	0·01144	0·01704	0·0596	0·422	10-1-36
Molassed	0·008	0·0100	0·0180	0·0842	0·532	,,

The foregoing results show very well that the total and the available nitrogen of the molassed plots are always greater than those in the unmolassed plots. Hence molasses acts as a nitrogen sparer in the soil and this is a very important application of molasses.

The above results also show that molasses can fix nitrogen in the soil even in presence of ammonium salts, as the total nitrogen in the soil containing molasses and ammonium sulphate is greater in the end than in the beginning.

The following experiments showing the retarding influence of cane sugar on nitrification and nitrogen loss from soils containing ammonium sulphate were carried on in open enamelled dishes:—

TABLE XIV.

Original soil contained 0·00356% NH_3-N, 0·0021% nitric$-N$, 0·0466% total N and 0·5134% C.

		Time of exposure.		
		62 hours.	132 hours.	200 hours.
1. 200 G. soil + 16 g. cane sugar	NH_3-N =	0·005%	0·0070%	0·0084%
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·05	0·0498	0·0499
	Total$-C$ =	4·221	3·187	1·882
2. 200 G. soil + 16 g. cane sugar + 8g. Na_3PO_4	NH_3-N =	0·00582	0·00728	0·0089
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·484	0·0498	0·0499
	Total$-C$ =	4·00	3·178	1·761
3. 200 G. soil + 16g. cane sugar + 0·04 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·0875	0·0668	0·0624
	NO_3-N =	0·0028	0·0028	0·0030
	Total$-N$ =	0·1842	0·175	0·148
	Total$-C$ =	4·114.	2·991	1·892
4. 200 G. soil + 16g. cane sugar + 0·4g. N as $(NH_4)_2SO_4$ + 8 g. NO_3PO_4	NH_3-N =	0·08824	0·0642	0·0604
	NO_3-N =	0·0028	0·0028	0·0030
	Total$-N$ =	0·2002	0·178	0·152
	Total$-C$ =	4·128	2·991	1·88
5. 200 G. soil + 16g. cane sugar + 2 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·028	0·017	0·0156
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·116	0·1112	0·1167
	Total$-C$ =	4·112	3·019	1·885
6. 200 G. soil + 16g. cane sugar + 0·2 g. N as $(NH_4)_2SO_4$ + 8 g. Na_3PO_4	NH_3-N =	0·0291	0·014	0·015
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·1169	0·1181	0·1172
	Total$-C$ =	4·121	3·029	1·721
7. 200 G. soil + 16g. cane sugar + 0·1 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·01	0·00934	0·00932
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·0934	0·0934	0·0934
	Total$-C$ =	3·914	2·871	1·895
8. 200 G. soil + 16g. cane sugar + 0·1 g. N as $(NH_4)_2SO_4$ + 8 g. Na_3PO_4	NH_3-N =	0·01	0·00922	0·0091
	NO_3-N =	0·0028	0·0028	0·0029
	Total$-N$ =	0·9333	0·057	0·0944
	Total$-C$ =	3·992	2·881	1·778
9. 200 G. soil + 0·4 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·04516	0·0233	0·02024
	NO_3-N =	0·00362	0·00388	0·00422
	Total$-N$ =	0·1346	0·123	0·0928
	Total$-C$ =	0·5068	0·5068	0·506
10. 200 G. soil + 0·2 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·0232	0·014	0·01336
	NH_3-N =	0·00278	0·005	0·00516
	Total$-N$ =	0·1072	0·1060	0·0875
	Total$-C$ =	0·5068	0·5068	0·5068
11. 200 G. soil + 0·1 g. N as $(NH_4)_2SO_4$	NH_3-N =	0·00822	0·0082	0·0082
	NH_3-N =	0·00406	0·005	0·005
	Total$-N$ =	0·0778	0·0772	0·07
	Total$-C$ =	0·5068	0·5068	0·5068

The foregoing results show that the total nitrogen in vessels containing cane sugar and ammonium sulphate is always greater than in the corresponding ones containing ammonium sulphate alone. Thus cane sugar acts as a sparer of the soil nitrogen. It has been generally believed that organic substances like sugars when added to soil causes anærobic denitrification but in none of our experiments, we observed any denitrification of this type with molasses or cane sugar added to the soil, which is exposed to light and air.

According to Lyon and Wilson (Cornell University Agricultural Experiment Station Memoirs, 1928, 115) nitrogen balance is not maintained but loss of nitrogen takes place when the crops grown during autumn only are ploughed in followed by a summer fallow. On the other hand, gain of nitrogen is observed in the soil under grass and not disturbed for summer fallow. The observations of Howard and Wad ("Waste Products of Agriculture," 1931, p. 100) show that a certain amount of nitrogen fixation also takes place in the composting of the waste products of agriculture according to the Indore method of composting, when the aeration in the compost heaps is sufficient. It appears that in the oxidation of the carbonaceous substances in the compost heaps, energy is liberated as is evident from the heat produced in these heaps and a part of this energy of oxidation is utilised in the fixation of nitrogen. It has been reported that when molasses is added to growing plants, harmful results are produced. This can be easily explained from the following considerations:—

The small amounts of nitrate, which is the real plant food present in the soil, reacts with the carbohydrates present in the molasses with the formation of ammonium salts through the agency of bacteria as is well known, or light as established by Dhar and Mukherji. Moreover, the ammonium salts may be eaten up by the increased growth of the micro-organisms caused by the addition of energy-rich carbohydrates of the molasses. In this way the available nitrogen of the soil may be lost to the crops. Moreover, the oxidation of the carbohydrates generates heat in the soil and both these results may be prejudicial to the growth of plants. The workers at Java have shown empirically that the carbohydrates present in the molasses were the real factors in improving soil fertility, because the effect produced by an equivalent amount of potash, phosphates, lime and combined nitrogen is insignificant. The experience of workers in other sugar producing countries shows that an interval of some weeks between the addition of molasses to the soil and the growth of crops on this soil seems necessary.

From our results it is clear that sufficient time is necessary for the oxidation of carbohydrates added with molasses leading to the maximum amount of ammonia formation and increase of total nitrogen in the soil. The carbohydrates must be oxidised in order that the nitrogen may be fixed and as this process takes time, an interval of 8 to 12 weeks, depending on the amounts of molasses added, is absolutely necessary.

The workers at Java have reported the formation of organic acids in the incipient stage after the addition of molasses to the soil. This observation has been confirmed by Vhaskaran and Narasimhamurti, Subrahmanyan and Sundara Ayengar (*Proc. Indian Acad. Sci.*, 1934, 1, 155) who have reported the production of acetic acid, propionic acid, butyric acid etc. under water logged conditions. We have observed that traces of alcohol and small amounts of organic acids are produced when molasses or cane sugar are added to the soil in presence of air, but a good deal of the sugars added with molasses is oxidised completely to carbon dioxide and water. Most of the intermediate products are also energy-rich and are oxidised to carbon dioxide in course of time on the soil surface. Hence large amounts of energy are available for the fixation of atmospheric nitrogen in the soil on the addition of molasses and proper æration.

Molasses in the Reclamation of Alkali Soils.

A systematic investigation is in progress in these laboratories for the reclamation of alkali soils by the application of molasses. It is well known that molasses contain between 60 to 65% carbohydrates, 4·5% potash, 2% lime, 0·5% phosphoric acid, 0·5% silica, 0·5% iron and aluminium oxides and 0·5% combined nitrogen and the rest, water. Moreover, molasses is distinctly acidic. Research work carried on in Allahabad, Bangalore, Java, and Hawaii shows that when molasses is added to the soil, along with carbonic acid, organic acids, like acetic, propionic, butyric, lactic etc., are produced in the early stages of the decomposition and partial oxidation of the carbohydrates present in molasses. Consequently the acids present in molasses and those obtained from the decomposition and partial oxidation can neutralise the alkali of the soils rich in alkali. Moreover, the carbonic acid, which is produced in large amounts from the decomposition and oxidation of carbohydrates, can convert the sodium carbonate of the alkali soils into bicarbonate. Also, in the processs of the escape of carbon dioxide from the molassed soil, the latter is rendered porous and its tilth is improved. Our researches show definitely that the moisture content of the molassed soil, is appreciably higher than that of the unmolassed one. The lime which is added to the soil along with molasses is rendered soluble by the organic acids formed from the molasses and is helpful in the conversion of the sodium soil into the calcium one. Molasses when added to soil also increases the total nitrogen, ammonia contents, the micro-organisms, the humus water retention capacity and the calcium salts, which are readily soluble. All these factors go towards the reclamation of the alkali soils on the addition of molasses. The soluble calcium salts are helpful in the improvement of the soil tilth by their precipitation power on the clay particles. Moreover, in presence of soluble calcium salts, the permeability of the soils is greatly improved.

Molasses to the extent of 100-300 maunds per acre has been applied to some alkaline fields near Cawnpore, Allahabad and Mysore and beneficial results in their reclamation have been obtained. Our results show that molasses is a better reclaiming agent for alkaline lands than either gypsum or powdered sulphur There is nitrogen loss for soils when these latter reclaiming agents are added to the alkaline lands, whilst molasses adds nitrogen. The reclaiming effect of molasses is much quicker than that of gypsum or powdered sulphur.

Influence of Ammonium salts and Nitrates on the Nitrogen Fixation in Soils by the Addition of Molasses.

A very important fact has been brought out by our researches namely, that the amount of ammonium salts obtained by fixation depends on the quantities of the available and possibly total nitrogen originally present in the soil before the addition of molasses or cane sugar. Thus in our first set of experiments with pure cane sugar when added to unsterile soil and exposed to sunlight, the ammoniacal nitrogen rose to 0·0186% from 0·00126% originally present in the soil, which contained 0·00164% available nitrogen In the second series of experiments the ammoniacal nitrogen increased from 0·00192% to 0·0162% and the total available nitrogen in the soil was 0·00392%.

Similarly with molasses, the fixation was less as it cantained some ammonium salts.

Our results show that in presence of ammonium sulphate or potassium nitrate, the fixation of atmospheric nitrogen in the soil on the addition of cane sugar and molasses may be small.

It appears, therefore, that in soils, containing a larger percentage of available nitrogen, the fixation due to the addition of energy rich compounds is less marked. In tropical countries, however, the nitrogen fixation on the addition of molasses or other carbonaceous compounds is likely to be always prominent, as the ammonia and total nitrogen contents of tropical soils are low.

Efficiency of the Nitrogen Fixation Processes of Different kinds.

It is well known that approximately 1% of the energy available in the oxidation of carbohydrates is utilised in the fixation of nitrogen in presence of Azotobacter In Table III it will be seen that the efficiency of nitrogen fixation in the induced oxidation of glucose or cane sugar in presence of ferrous hydroxide is of the same order as in the bacterial fixation. Further work on the efficiency of bacterial, photochemical and catalytic nitrogen fixation is in progress.

It appears that a large amount of molasses produced in the country has to be applied in agriculture for improving sugarcane, rice, wheat and other products. Our experiments show that molasses can serve as an excellent fertiliser in the cultivation of rice and other crops, thus by the application of 3600 kilograms of molasses per acre of land and digging and watering the soil once every week for two months (May and June 1935), 14·1 maunds of *Aus* paddy and 26·9 maunds of straw were obtained in the molassed land, while 8·5 maunds paddy and 22·4 maunds straw were grown in the control land.

SUMMARY.

1. When cane sugar solutions and sterilised soil are exposed to sunlight for a long time in quartz vessels under sterile conditions, there is appreciable increase in the available and total nitrogen consents of the sterile soil.

2. Experiments show that 4 mg. of nitrogen are fixed as ammonia per gram of glucose or cane sugar oxidised by passing air through solutions of these carbohydrates in presence of ferrous hydroxide. It appears that the efficiency of nitrogen fixation obtained in the induced oxidation of carbohydrates is of the same order as that with cultures of Azotobacter thriving in flasks containing solutions of energy-rich compounds.

3. When cane sugar solution is added to ordinary soils and exposed to sunlight and air, the ammoniacal and total nitrogen are increased.

4. When molasses in different amounts are added to soils in dishes and exposed to sunlight and air, the ammoniacal and total nitrogen are also increased. This increase of nitrogen is always greater in sunlight than in the dark.

5. Our experimental results show that in the photochemical or induced oxidation of carbohydrates, nitrogen fixation can take place. The oxidation of energy-rich organic compounds by air, either by light absorption or by chemical induction or by bacterial action, causes the fixation of atmospheric nitrogen. It appears, therefore, that in tropical countries in ordinary soils, the fixation of atmospheric nitrogen by the addition of energy-rich compounds is partially bacterial and partially photochemical and catalytic.

6. Field experiments with molasses when mixed with soil, show that there is an appreciable increase in the total nitrogen and ammoniacal nitrogen contents. The amount of ammoniacal nitrogen goes on increasing up to a limiting value when it decreases. But at this stage, the nitric nitrogen increases due to the oxidation of the ammonium salts formed from nitrogen fixation, and the C : N ratio tends to approach the normal value. This is the time when crops are to be sown on the molassed fields. Using 10800 kg. of molasses per acre of land and digging or turning over once in 10 days, the land is ready for crops in about 12 weeks; with 3600 to 7200 kilogram per acre it is suitable in about 8 weeks. In all our field trials with molasses as a fertilizer, we have always observed an increase of total and available nitrogen. Moreover, as molasses contain potash, phosphate, lime and as nitrogen is fixed in molassed lands, it is an excellent fertilizer for tropical soils.

7. The moisture contents of molassed lands are always greater than in the unmolassed ones.

8. Excellent composts containing double the amount of total nitrogen as is originally present in the soil have been obtained by mixing molasses with soil in heaps, which are exposed to air and light.

9. The available and total nitrogen of soils, which have been molassed for two consecutive years, are greater than in soils molassed once. It seems, therefore, that molasses exerts residual effect on the soil.

10. This new method of nitrogen fixation based on the principle of the utilisation of the energy available from the oxidation of carbohydrates and other organic compounds in the soil should be largely

utilised in tropical countries, where the velocity of the oxidation of substances in the soil is high under ordinary conditions due to the high temperatures and light absorption.

11. In cold countries, the soil temperature being low and due to the lack of sunshine, the velocity of the oxidation of energy-rich substances present in the molasses may be small and thus the energy available from the oxidation of carbohydrates may be too small for any marked nitrogen fixation. Moreover in temperate climates, Azotobacter is not suitable for nitrogen fixation, as our experiments and those carried on in other countries show that nitrogen fixation by Azotobacter at 10° and lower temperatures is practically nothing and Azotobacter requires more heat than most other bacteria and that is why Azotobacter has not been utilised by agriculturists in cold countries for nitrogen fixation.

12. Azotobacter should be widely utilised in the fixation of atmospheric nitrogen in the soil of tropical countries when fed with energy-rich substances like molasses, press cakes etc.

13. Our results obtained with ammonium sulphate added to the soil with and without molasses show that the total and available nitrogen of the molassed plots are always greater than those in the unmolassed plots. Hence molasses not only fix nitrogen in the soil but also act as a sparer of nitrogen in the soil and this is a very important application of molasses.

14. Cane sugar has also been found to act as a sparer of soil nitrogen. When molasses or cane sugar is added to the soil exposed to light and air, there is no evidence of anærobic denitrification in all our experiments, although it has been generally believed that in such cases, anærobic denitrification sets in.

15. Molasses has been found to be a better reclaiming agent for alkaline fields than gypsum or powdered sulphur.

16. It seems probable that nitrogen fixation takes place in animal or plant respiration.

17. It appears that in ærobic nitrogen fixation through the agencies of bacteria, light and chemical induction, the nitrogen and oxygen combine forming nitrate, which in its turn is converted into ammonia and small amounts of amino acids.

18. Greater yields of rice and sugarcane have been obtained with molasses as a manure.

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Oxidation of Nitrites to Nitrates in Sunlight

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In a communication to *Nature* (1934, **133**, 213) it was reported that dilute aqueous solutions of alkali nitrites are oxidised to the nitrate in presence of catalysts like ZnO, TiO_2, Fe_2O_3, etc., when exposed to sunlight. These observations are of great importance in view of the fact that the soil contains nitrates and not nitrites under normal conditions.

We have carried on further experiments on the photo-oxidation of solutions of sodium nitrite of different concentrations in presence of photocatalysts and some of our results are recorded in this communication.

The estimation of the nitrite was carried on colorimetrically using the well known α-naphthylamine-sulphanilic acid test. A Duboscq colorimeter was utilised for this purpose. The total nitric nitrogen was estimated by reducing the solution with alkali and Devarda's alloy and distilling off the ammonia which was absorbed by standard solutions of sulphuric acid. The ammonium salt formed was estimated colorimetrically by Nessler's reagent and this was checked by estimating the excess of sulphuric acid by standard solutions of caustic soda using methyl red as an indicator.

EXPERIMENTAL.

50 C.c. of the nitrite solutions were exposed to sunlight along with 0·5 g. of the photocatalyst in open 400 c.c. Jena glass breakers. The solutions were frequently stirred when exposed to sunlight for five hours every day. Several sets of beakers containing solutions of different concentrations of the nitrite were exposed and in each estimation the total amount contained in a beaker was made up to 100 c.c. 80 C.c. of this diluted solution were employed for the total nitrogen estimation, while 20 c.c. were reserved for nitrite estimation by the colorimetric method. The following results were obtained

TABLE I.

The original soln. of $NaNO_3$ contained 0·0348 g. of N per 100 c.c.

Photocatalysts.	Amount of NO_2-N in g./100 c.c. after an exposure of			
	30 hours.	60 hours.	90 hours.	120 hours.
Fe_2O_3	0·01137	0·011	0·01	0·0089
ZnO	0·0133	0·01025	0·00471	0·00141
Soil	0·01541	0·01532	0·0136	0·0133
TiO_2	0·0137	0·0115	0·00762	0·0058

The foregoing results show that amongst the photocatalysts examined, namely Fe_2O_3, ZnO, Soil, TiO_2, zinc oxide is the best reagent in accelerating the photo-oxidation of nitrite solutions to nitrate. Solutions of nitrite containing no photocatalyst were also exposed but very little oxidation was observed in any of them.

In the following table the results obtained with ZnO as the photocatalyst are summarised. Four different concentrations of sodium nitrite solutions were taken to start with, *viz.*, $N/10{\cdot}2=0{\cdot}0686$ g.; $N/20{\cdot}4=0{\cdot}0343$; $N/40{\cdot}8=0{\cdot}01710$; $N/81{\cdot}6=0{\cdot}00855$ of NO_2-N per 100 c.c.

TABLE II.

Amount of NO_2-N and total N expressed in g/100 c.c. and exposed for different periods. The solutions were always tested for ammonia also after the exposure, but in no case was it detected.

Original amount to start with.		20 hours.		40 hours.	
NO_2-N.	Total N.	NO_2-N.	Total N.	NO_2-N.	Total N.
0·0686	0·0686	0·0648	0·0684	0·06034	0·0684
0·0343	0·0343	0·0280	0·03452	0·0234	0·03398
0·0171	0·0171	0·00934	0·016464	0·003226	0·015992
0 00855	0·00855	0·00108	0·00848	Nil	0·00848

Original amount to start with.		60 hours.		80 hours.	
NO_2-N.	Total N.	NO_2-N.	Total N.	NO_2-N.	Total N.
0·6686	0·0686	0·050	0·0684	0·0432	0·0684
0·3343	0·0343	0·01522	0·03396	0·007610	0·03410
0·0171	0·0171	0·000060	0·01598	Nil	0·0162
0·00855	0·00855	Nil	0·00848	Nil	0·00848

The amount of nitrate nitrogen formed by oxidation of nitrite nitrogen can be obtained by deducting the amount of nitrite nitrogen from the corresponding amount of total nitrogen. The results are tabulated below.

TABLE III.

Original amount of NO_2-N in g./100 c.c.	Amount of NO_2-N in g./100 c.c. after an exposure of 20 hours.	40 hours.	60 hours.	80 hours.
0·0686	0·0036	0·00806	0·0184	0·0252
0·0343	0·00652	0·01058	0·01874	0·02649
0·0171	0·007124	0·012766	0·01592	0·0162
0·00855	0·0074	0·00848	0·00848	0·00848

Some beakers containing 50 c.c. of $N/81{\cdot}6$-$NaNO_2$ along with 0·5 g. of ZnO were kept in the dark and analysed after 16 days (the time taken up by these experiments). In none of these beakers any nitrite was converted into nitrate.

The foregoing results show that sodium nitrite of concentration varying from $N/10{\cdot}2$ to $N/81{\cdot}6$ are readily oxidised to the nitrate when exposed to light in presence of ZnO. In the more concentrated solutions, the amount of oxidation is less, but in the dilute solutions even after 40 hours' exposure, the oxidation of the sodium nitrite to sodium nitrate is complete. It is clear, therefore, that aqueous solutions of nitrite when exposed to light and air undergo the following reversible change

$$2NaNO_2 + O_2 \rightleftharpoons 2NaNO_3.$$

In dilute solutions the chemical change proceeds from left to right and in strong solutions from right to left, *i.e.*, concentrated solutions of $NaNO_3$ when exposed to light are decomposed into sodium nitrite with liberation of oxygen, but dilute solutions of sodium nitrite when exposed to air and light are readily oxidised to sodium nitrate.

It may be argued that these solutions exposed to sunlight in open beakers might have been contaminated with the nitrate-formers (Nitrobacter). In many of our experiments after the necessary exposure we attempted to detect the presence of nitrate-formers microscopically but in no case the nitrobacter was obtained and hence it is believed that these oxidations of sodium nitrite to nitrate taking place in presence of light are due to light absorption and not to bacteria. At the same time the fact, believed by most of the bacteriologists that strong sunlight is injurious for the growth of nitrate-formers, further eliminates the possibility of the presence of any nitrobacter cells in our nitrite solutions exposed to sunlight. It is well known that solutions of nitrite can absorb ultraviolet light copiously. If this nitrate formation were entirely a bacterial process, as has hitherto been believed, some conversion of the nitrite into the nitrate in the beakers kept in the dark soould have taken place, but it has already been stated that in these no nitrate has been formed.

This photo-oxidation of sodium nitrite to nitrate also takes place in presence of soil. Moreover, it is well known that small amounts of ammonium salts are always present in normal soils and these ammonium salts are oxidised to nitrite and finally to nitrate in the soil. Hence the amount of nitrite that can temporarily exist in the soil being small is readily oxidised to the nitrate stage. It is clear, therefore, that the process of nitrification, which has hitherto been considered due to bacteria alone can also be photochemical as our results show that dilute solutions of $NaNO_2$ are readily oxidised to sodium nitrate in presence of light and nitrite may exist temporarily in the soil only in the highly diluted state possibly adsorbed on the soil surface and undergoes oxidation readily to nitrate on the soil surface.

Hitherto it was universally believed that the conversion of nitrite to nitrate in soil takes place only through the agency of nitrate-formers. In view of our results given above, this universal application of bacterial agency to nitrate oxidation in soil can no longer be taken as a complete truth. In previous communications (*cf*. Dhar. " Influence of Light on some Biochemical Processes, 1935), we have already emphasised the importance of photochemical oxidations in relation to soil processes in tropical countries. The soil temperature in tropical countries in summer months during the day time goes much beyond the maximum temperature necessary for the growth of bacteria in general. In spite of this fact an increment in soil nitrate is always noticed in summer months in every locality of the world. The validity of the bacterial theory of nitrification and the observance of the increment in the nitrate content of the soil in summer months could not be reconciled until very recently. Now with the acceptance of our theory of photochemical nitrification, it becomes clear why the nitrate content of the soil is largest in the summer.

SUMMARY.

1. Aqueous solutions of sodium nitrite are oxidised to nitrate when exposed to sunlight in presence of photo-catalysts like ZnO, TiO_2, Fe_2O_3, soil etc.

2. The dilute solutions are completely oxidized to nitrate, whilst in stronger solutions, it seems the following equilibrium is attained :—
$2NaNO_2 + O_2 \rightleftharpoons NaNO_3$.

3. Zinc oxide has been found to be the best photocatalyst in this oxidation.

4. It appears, therefore, that Nitrobacter is not the only agency which can convert a nitrite to nitrate in the soil ; light may also perform the same function.

5. In tropical countries in summer months during the day time, the temperatures of the soil are generally much higher than the maximum temperature suitable for the existence of the Nitrobacter. At such times, it seems, the photochemical oxidation of nitrate is the more important process in tropics than the bacterial oxidation.

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Condensation of Chloral with Acid Amides. Properties of -CH(OH)·CCl_3 Group.

By (late) Andrew Norman Meldrum and Moreshwar Govind Bhojraj.

The present paper deals with the reduction by zinc and glacial acetic acid of the condensation products of chloral with some aliphatic and aromatic acid amides. The formula given by Yelburgi and Wheeler (*J. Indian Chem. Soc.*, 1925, **2**, 1) is applied to the products.

EXPERIMENTAL.

Condensation of the Amides with Chloral.—Chloral (a little excess over the molecular proportion) and the amides were mixed. The reaction was vigorous with acetamide, but with other amides the mixture required to be heated at 100°. The higher products are sticky. Excess of chloral and the unreacted amides were removed by triturating the solid with cold water. The product was crystallised from dilute alcohol.

Reduction of the Chloral Amides.—Zinc dust (2 mol.) was added gradually under stirring during 4-5 hours below 40° to the chloral amide in acetic acid. Zinc acetate began to separate as the reduction progressed and addition of more acetic acid was advisable to facilitate stirring. Finally zinc acetate was filtered off. With *iso*butyramide, phenylacetamide and benzamide, the filtrate gave the solid on dilution with water. It was then further purified. With other amides the filtrate was neutralised with caustic soda solution of moderate strength at below 40°. The product separated as an oil. If it did not solidify it was extracted with ether and distilled under reduced pressure. These products are soluble in cold and hot water and in most organic solvents. They are stable and distil without decomposition.

The properties of the new compounds are given in the following table.

Name.	Formula.	Crystallised from.	Appearance.	M.p.	Analysis	
					Found.	Calc.
β-Dichlorovinylacetamide	$C_4H_5ONCl_2$	Dilute alcohol	Rectangular plates	88—89°	C, 31·1 H, 3·3	31·1 3·3 *
Chloralpropionamide	$C_5H_8O_2NCl_3$	Alcohol	Thin plates	166—67°	Cl, 48·2	48·3
β-Dichlorovinylpropionamide	$C_5H_7ONCl_2$	Benzene + ligroin	Needles	100—101°	C, 35·5 H, 4·3	35·7 4·2*
Chloral *iso*butyramide	$C_6H_{10}O_2NCl_3$	Hot alcohol	Plates	156—57°	Cl, 45·3	45·4
β-Dichlorovinyl*iso*butyramide	$C_6H_9ONCl_2$	Dilute alcohol	Long needles	84—85°	38·8	39·0
Chloral-*n*-valeramide	$C_7H_{12}O_2NCl_3$	Alcohol	Leaf like plates	142°	42·7	42·8
β-Dichlorovinyl-*n*-valeramide	$C_7H_{11}ONCl_2$	Benzene + ligroin	Needles	65—66°	36·0	36·2
Chloral-*n*-capronamide	$C_8H_{14}O_2NCl_3$	Alcohol	Shining plates	139°	40·4	40·5
β-Dichlorovinyl-*n*-capronamide	$C_8H_{13}ONCl_2$	Benzene + ligroin	Needles	62—64°	33·7	33·8
Chloral-*n*-caprylamide	$C_{10}H_{18}O_2NCl_3$	Hot alcohol	Plates	125—26°	36·6	36·7
β-Dichlorovinyl-*n*-caprylamide	$C_{10}H_{17}ONCl_2$	Water	Needles	38—39°	29·6	29·8
β-Dichlorovinyl benzamide	$C_9H_7ONCl_2$	Benzene + ligroin	Rectangular plates	68—70°	C, 49·8 H, 3·3	50·0 3·3*
Chloralphenylacetamide	$C_{10}H_{10}O_2NCl_3$	Alcohol	Rhombic plates	141°	Cl, 37·5	37·7
β-Dichlorovinyl phenylacetamide	$C_{10}H_9ONCl_2$	Alcohol	Long flat prisms	90—92°	30·5	30·8

* (*cf.* Yelburgi and Wheeler, *loc. cit.*).

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Halogenation. Part XIV. Iodination of Aromatic Hydrocarbons and Bromotoluenes.

By Phuldeo Sahay Varma and C. Sreenivasmurthyachar.

The iodination of aromatic hydrocarbons in presence of (*i*) a mixture of fuming nitric acid and fuming nitrosulphonic acid or (*ii*) sodium nitrite and fuming sulphuric acid has been described in previous communications (Varma, Kulkarni and Panickar, *J. Indian Chem. Soc.*, 1926, **3**, 291, 342). In the present paper the iodination of aromatic hydrocarbons in presence of a mixture of fuming nitric acid and fuming sulphuric acid are described. In this reaction nitro compounds are also formed, but by using a small excess of fuming sulphuric acid, their formation is avoided.

The iodination of the three bromotoluenes in presence of nitrosulphonic acid (*vide* Varma and Venkatraman, *J. Indian Chem. Soc.*, 1935, **12**, 244) is also described. The mono-iodo compounds obtained are identical with the compounds obtained by previous workers by other methods (*cf.* Hurtz, *Ber.*, 1896, **29**, 1405 ; Cohen and Miller, *J. Chem. Soc.*, 1904, **85**, 1627 ; Wroblewski, *Annalen*, 1873, **168**, 164, 169).

EXPERIMENTAL.

Iodobenzene.—Benzene (15 c. c.), iodine (10 g.) and glacial acetic (20 c. c.) were heated under a reflux condenser on a water-bath and a mixture of fuming nitric acid (6 g.) and fuming sulphuric acid (8 g.) was added to the contents of the flask in portions of 10 drops at a time and the heating continued for 2½ hours. The product of the reaction was then washed free from acid, dried over calcium chloride and distilled ; 12 g. of iodobenzene, b. p. 186-189°, were obtained.

Toluene (15 c. c.), iodine (10 g.), fuming HNO_3 (5·4 g.), fuming H_2SO_4 (7·6 g.) ; yield 12·7 g. of *o*-iodotoluene.

p-Xylene (15 c. c.), iodine (10 g.), fuming HNO_3 (6·0 g.), fuming H_2SO_4 (7 g.) ; yield 8·5 g. of 2-iodo-*p*-xylene.

o-Xylene (15 c. c.), iodine (10 g.), fuming HNO_3 (4·8 g.), fuming H_2SO_4 (5·2 g.); yield 8·2 g. of 4-iodo-*o*-xylene.

m-Xylene (15 c. c.), iodine (10 g.), fuming HNO_3 (5·5 g.), fuming H_2SO_4 (6·7 g.); yield 11·8 g of 4-iodo-*m*-xylene.

Ethylbenzene (15 c. c.), iodine (10 g.), fuming HNO_3 (6·0 g.) fuming H_2SO_4 (7·6 g.); yield 2·3 g. of 4-iodoethylbenzene.

Pseudocumene (15 c. c.), iodine (10 g.), fuming HNO_3 (6·4 g.), fuming H_2SO_4 (7·6 g.); yield 2·0 c. c. of 5-iodopseudocumene.

2-*Bromo*-4-*iodotoluene*.—To a mixture of *o*-bromotoluene (5 c. c.), iodine (5 g.) and chloroform (10 c. c.) heated in a flask with a reflux condenser on a sand-bath, nitrosulphonic acid mixture (2·8 c.c.) was added drop by drop from the top of the condenser. The flask was heated for 6 hours at about 170-180°, allowed to cool, washed free of iodine by 2 % solution of sodium hydroxide, dried over fused calcium chloride and distilled. The product distilling between 265-267° was found to be pure 2-bromo-4-iodotoluene, yield 6·5 g.

3-*Bromo*-4-*iodotoluene*.—*m*-Bromotoluene (5 c. c.), iodine (5 g.), glacial acetic acid (15 c. c.) and chloroform (10 c. c.) were heated on a sand-bath in a flask for 10 minutes. When the contents began to boil, nitrosulphonic acid mixture (3 c. c.) was added in a portion of 0·5 c. c. every 10 minutes. The flask was heated on the whole for 4 hours at about 180-190°. The product was purified as in the preceding case and the fraction distilling between 265-267° was identified to be 3-bromo-4-iodotoluene, yield 7·4 g.

4-*Bromo*-2-*iodotoluene*.—*p*-Bromotoluene on similar treatment gave 4-bromo-2-iodotoluene (3·4 g.) distilling at 262-267°.

CHEMICAL LABORATORIES,
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Halogenation. Part XV. Chlorination and Bromination of Cumene and *p*-Cymene.

By Phuldeo Sahay Varma and M. K. Srinivasan.

p-Chloro- and *p*-bromocumenes as well as 2-chloro-*p*-cymene and 2:5-dichloro-*p*-cymene have been obtained by the action of the halogens on the hydrocarbons in presence of iodine or aluminium chloride (Genvresse, *Bull., Soc. chim.*, 1893, *iii*, **9**, 223; Jacobson, *Ber.*, 1879, **12**, 430; Gerichten, *Ber.*, 1877, **10**, 1249; Junger and Klages, *Ber.*, 1896, **29**, 314). Among the side-chain compounds, 1′-bromocumene has been obtained by direct bromination (Wheeler and Johnson, *J. Amer. Chem. Soc.*, 1902, **24**, 680) while 1′-chloro-, 1′:2′-dibromo- and 1′:2′-dichlorocumenes have been obtained by indirect methods only, whereas chlorination of *p*-cymene even under conditions most favourable for side-chain substitution, has been reported to result mostly in nuclear substitution, giving very poor yields of side-chain substituted derivatives (Quist, Forth III nord, Kemistmotet, 1928, 194). The present work was undertaken to investigate in full the action of chlorine and bromine on cumene and *p*-cymene in sunlight as well as in presence of halogen carriers such as aluminium chloride, ferric chloride, palladium chloride, lithium bromide, vanadium trioxide, iron, aluminium, tungsten, selenium, tellurium, thallium, sulphur, antimony, pyridine, etc. Working in sunlight 1′:2′-dichloro-, 1′-bromo- and 1′:2′-dibromocumenes have been prepared. In diffused daylight chloro- and bromocumenes and the following new di- and mixed halogen derivatives have been obtained :—(*i*) *p*-chloro-1′-chlorocumene, (*ii*) *p*-bromo-1′-bromocumene and (*iii*) *p*-chloro-1′-bromocumene. By brominating 2-chloro-*p*-cymene a new chloro-bromo derivative, 2-chloro-5-bromo-*p*-cymene, has been obtained.

EXPERIMENTAL.

p-Chloro-1′-chlorocumene.—Through cumene (10 c. c.) containing 1 c. c. of a 15% solution of iodine in acetic acid pure chlorine gas was passed for about 6 hours in diffused sunlight. The solid product was removed by filtration, dried, extracted with benzene, washed free of chlorine and crystallised, m. p. 180° ; yield 1·1 g. (Found : Cl, 36·97 $C_9H_{10}Cl_2$ requires Cl, 37·23 per cent). The liquid portion was washed free of chlorine, dried and distilled under reduced pressure and was found to be 4-chlorocumene (3 c. c., b. p. 122-124°/12 mm.). The solid product gave on oxidation *p*-chlorobenzoic acid. Hence the second chlorine atom must be in the side-chain. Since substitution takes place with the elimination of hydrogen attached to the carbon

Halogenation. Part XVI. Bromination and Iodination of Mesitylene.

By Phuldeo Sahay Varma and T. S. Subrahmanian.

The present paper describes the bromination of mesitylene in presence of fuming nitric acid and the iodination of mesitylene in presence of nitro-sulphonic acid mixture. The substances obtained are the mono-, di- and tri-bromo- and mono-, di- and tri-iodo derivatives of mesitylene. These were identified with the products obtained by the previous workers by other methods (Fittig and Storer, *Annalen*, 1868, **147**, 6; Schram, *Ber.*, 1886, **19**, 212; Tohl, *Ber.*, 1892, **25**, 1522; Tohl and Echel, *Ber.*, 1893, **26**, 1100.)

Iodination of 2-bromomesitylene in presence of nitrosulphonic acid mixture yields the hitherto undescribed 2-bromo-4-iodomesitylene.

EXPERIMENTAL.

2-*Bromomesitylene.*—To mesitylene (10 c.c.) in a flask, bromine (3·5 c.c.) was added drop by drop in about 30 minutes. Fuming nitric acid (3·5 c.c.) was then added to it in the cold slowly and the mixture allowed to stand for about 2 hours. The product was washed free of bromine by 2% sodium hydroxide solution, dried and distilled. The unused mesitylene distilled over first and then the mono-bromomesitylene (7·5 c.c.) at about 224°. When the same experiment was repeated either on a water-bath or on a sand-bath the resulting compound was very much contaminated with the nitro-derivatives.

2:4-*Dibromomesitylene.*—To mesitylene (5 c.c.) and acetic acid (5 c.c.), bromine (3·5 c.c.) was added with shaking. Fuming nitric acid (2 c.c.) was then added and allowed to stand for about 2 hours. The product was extracted with carbon tetrachloride, washed free of bromine, dried and allowed to crystallise. Needle-shaped crystals (5·6 g.), m.p. 62°.

2:4:6-Tribromomesitylene.—The previous experiment was repeated using 5·2 c.c. of bromine and 1 c.c. of fuming nitric acid and the product worked up as before. It (8·0 g.) melted at 222°.

2:4-Diiodomesitylene.—Mesitylene (5 c.c.), iodine (5·5 g.) and glacial acetic acid (5 c.c.) were taken in a flask and refluxed on a water bath. Nitrosulphonic acid mixture (3 c.c.) was added drop by drop and heated for 3 hours. The product was extracted with benzene, washed free of iodine, dried and the benzene and the unused mesitylene distilled over. The residue in the distilling flask was crystallised from rectified spirit as white needles (4·5 g.), m.p. 82°-83°.

2:4:6-*Tri-iodomesitylene* has been obtained from 2:4-diiodomesetylene (4 g.), iodine (5 g.), acetic acid (10 c.c.) and nitrosulphonic acid (5 c.c.) by the preceding method. White flaky crystals (6·5 g.), m.p. 208°.

2-Bromo-4-iodomesitylene.—2-Bromomesitylene (5 c.c.) was iodinated as mentioned above with iodine (5 g.), acetic acid (15 c.c.) and nitrosulphonic acid mixture (5 c.c.) on a sand-bath for about an hour and a half. On cooling, a shining white solid mass separated out. It was removed from the rest of the liquid and extracted with benzene. The benzene extract was washed free of iodine by shaking with 5% solution of sodium hydroxide and then with water, dried over fused calcium chloride and the excess of benzene distilled off. On allowing the solution to cool, white needle-shaped crystals (4 g.) separated out. On crystallisation from benzene it melted at 175-76°. It is soluble in alcohol and benzene. (Found: Total halogen, 64·10. $C_9H_{10}BrI$ requires Total halogen, 63·68 per cent).

CHEMICAL LABORATORIES,
HINDU UNIVERSITY, BENARES.

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Parachor and Chemical Constitution. Part V. The Structure of "Liquid Crystals".

By Susil Kumar Ray.

Inspite of a great amount of investigations on the structure of the anisotropic liquids, the initial change of these substances on heating into the mesomorphic or cloudy state is not yet clearly understood. The work of Vorlander, Bose and various other investigators have shown that on melting, the cohesion between the molecules, which previously held them in the crystal arrangement, does not break down uniformly in all directions. There may be a lateral cohesion which still exists, which will tend to hold the molecules in bundles. This makes the liquid anisotropic. It was thought that the determination of the parachor of these substances at different temperatures might be helpful in the elucidation of this problem. From a perusal of the literature it was found that Jager (*Z. anorg. Chem.*, 1917, **101**, 1) determined the surface tension and density of some of these compounds over wide ranges of temperatures. In the present paper the parachor of these substances has been calculated from Jager's data, and an attempt has been made to explain the change from the mesomorphic state to the clear liquid state from a knowledge of the parachor.

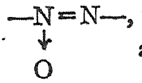
In the following tables the parachor of azoxybenzene, *p*-azoxyanisole, *p*-azoxyphenetole and *p*-methoxybenzalazine at different temperatures have been calculated. Though azoxybenzene is not a liquid crystal, its parachor is given as a basis for comparison. In the last column of the Tables I, II, and III the parachor has been calculated on the assumption that the azoxy compounds contain the grouping  $-\underset{\overset{\downarrow}{O}}{N}=N-$, which is the accepted structure for the azoxy compounds and is confirmed from the results in Table I.

Table I.

Azoxybenzene.

$P_{\text{calc.}} = 446{\cdot}6$.

Temp.	Surface tension.	Density.	$P_{\text{obs.}}$	Temp.	Surface tension.	Density.	$P_{\text{obs.}}$
55·8°	39·3	1·133	437·5	115°	34·7	1·087	442·2
70·6	38·3	1·121	439·4	130·5	33·5	1·074	443·5
85·0	37·1	1·110	440·2	145·5	32·1	1·063	443·3
100	35·9	1·098	441·5	162	30·8	1·050	444·2

TABLE II.

p-*Azoxyanisole.*

$P_{\text{calc.}} = 564{\cdot}6$

Temp.	Surface tension.	Density.	$P_{\text{obs.}}$	Temp.	Surface tension.	Density.	$P_{\text{obs.}}$
115°	40·1	1·171	554·6	144·5°	37·2	1·136	561·0
120	39·0	1·166	552·0	155·2	36·0	1·126	561·5
126	37·7	1·159	550·7	160·5	35·5	1·124	560·7
129·5	36·4	1·156	548·6	174·5	34·2	1·112	561·3
133·5	37·8	1·152	555·6	190	33·0	1·100	562·3
138·1	37·9	1·142	560·8	211	31·4	1·080	565·7

TABLE III.

p-*Azoxyphenetole.*

$P_{\text{calc.}} = 642{\cdot}6.$

Temp.	Surface tension.	Density.	$P_{\text{obs.}}$	Temp.	Surface tension.	Density.	$P_{\text{obs.}}$
142·5°	31·6	1·094	620·3	168·5°	29·3	1·068	623·6
147·5	30·7	1·089	618·6	174·5	28·6	1·053	628·7
151·8	30·0	1·084	618·0	190	27·3	1·039	629·5
159	29·0	1·076	617·3	205	26·2	1·026	631·4
164	28·3	1·072	615·9	219	25·2	1·014	632·5

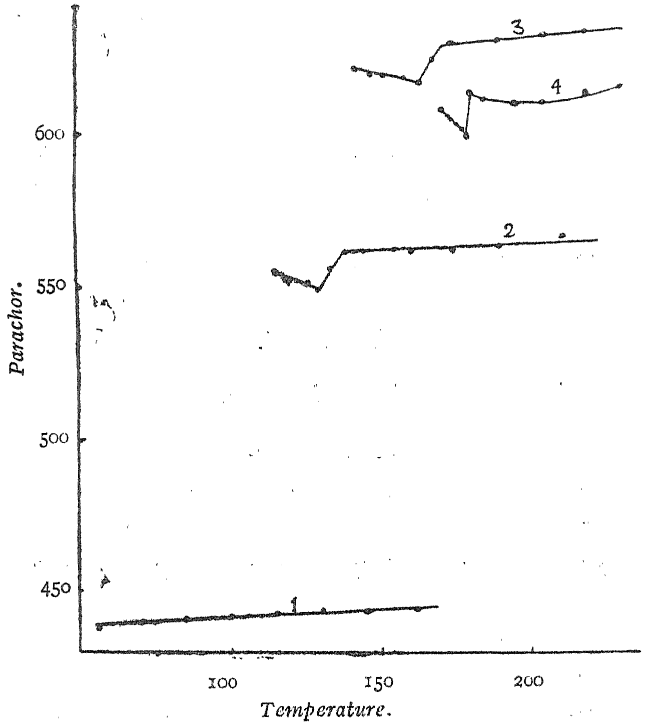
TABLE IV.

p-Methoxybenzalazine.

$P_{\text{calc.}} = 613{\cdot}2.$

Temp.	Surface tension.	Density.	$P_{\text{obs.}}$	Temp.	Surface tension.	Density.	$P_{\text{obs.}}$
171°	32·1	1·051	607·1	180·5°	31·2	1·035	612·4
173·5	31·4	1·049	604·9	185	30·4	1·031	610·6
174·5	31·1	1·048	604·0	195	29·2	1·023	609·2
176·5	30·5	1·046	602·3	204·5	28·3	1·015	609·4
178	29·9	1·044	600·5	219	27·4	1·002	612·3
179	29·4	1·043	598·5	230·5	26·8	0·993	614·4

The variation of the parachor with temperature becomes strikingly evident from the following curves drawn by plotting $P_{obs.}$ against the corresponding temperatures (the number of the curves corresponds with that of the table).



It will be observed from the above tables and the curves, that the parachor of the liquid crystals varies with the temperature. The parachor at first decreases gradually, reaches a minimum value and then just a few degrees before the transition point it increases abruptly and attains a value about 12-14 units higher at the true melting point and then increases gradually with the increase of temperature. This abrupt rise in the parachor can only be explained on the assumption that in the mesomorphic state the molecules are greatly associated. No other constitutional change in the molecule will be sufficient to account for this rise of about 12 units in the parachor. As the true melting point is reached, the lateral cohesion which still exists between the molecules, breaks down and the molecules become less complex. This increase of about 12 units in the parachor at the transition point can easily be explained on the assumption that in the mesomorphic state seven or eight molecules are associated to form a complex molecule (for then the parachor decrease will be 7 × 14·4/8 or 12·6 units, Sidgwick, *J. Chem. Soc.*, 1930, 1461). The variations in the parachor at temperatures above the melting point may be explained on the assumption that the molecules are still slightly associated, and this association diminishes with the rise of temperatures; with azoxybenzene this phenomenon is also observed.

My grateful thanks are due to Prof. P. R. Ray of the University College of Science and to Prof. A. Maitra of the Presidency College for their kind interest.

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Negative Ferric Hydroxide Sol. A Modified Method of its Preparation.

BY ASHUTOSH DAS AND RAJENDRALAL DE.

Powis (*J. Chem. Soc.*, 1915, **107**, 818) describes a simple method for the preparation of negative ferric hydroxide sol. This sol contains, however, an excess of alkali which evidently has a stabilising influence on it. Our attempt was directed to replace the superfluous alkali by another electrolyte, neutral in character, and possessing at the same time a stabilising influence on the sol. We required such a neutral sol for extracting uranium-X from uranyl salts. In this attempt we have found a few electrolytes possessing stabilising action. They are characterised from the other (similarly examined) electrolytes in giving iron salts, stable in an alkaline medium. It is generalised therefrom that an electrolyte, which gives an iron salt, stable in an alkaline medium, has a stabilising action on negative ferric hydroxide sol.

The substances found to possess a stabilising action are potassium citrate, potassium tartrate, potassium carbonate, potassium sulphide, sodium phosphate and sodium silicate. The citrate and the tartrate are already known to possess such stablising action with regard to negative ferric hydroxide sol. The neutrality in all cases has been tested with litmus. The sol obtained with potassium sulphide was, however, faintly alkaline.

The nature of the different sols have been tested by their behaviour as regards preciptation towards a normal solution of barium chloride, lanthanum nitrate or potassium sulphate.

EXPERIMENTAL.

For preparing a sol according to Powis (*loc. cit.*), to 150 c.c. of $N/100$-alkali hydroxide solution, 100 c.c. of $N/100$-$FeCl_3$ solution were added drop by drop, and the alkali hydroxide continuously shaken. It is, however, possible to add more of ferric chloride solution to the alkali hydroxide, but by this addition at a definite stage the ferric hydroxide present in the sol condition, is thrown out of the solution. There exists, therefore, a definite ratio (as will be evident from Fig. 1) between the amounts of the alkali and the ferric chloride used up when the precipitation phenomenon occurs. If the stabilising electrolytes be added before introducing ferric chloride, the above ratio changes and the precipitation occurs at a later stage; by increasing the amount of a stabiliser precipitation may be made to take place just after the equivalent amount of ferric chloride has been added. There exists, therefore, a definite limit in the amount of a stabiliser, which enables an equivalent amount of iron to remain in the sol condition. And if more than this limiting amount be taken at the beginnig and then the equivalent amount of ferric chloride be added, the required neutral sol will be obtained.

With substances possessing no stabilising action, the definite ratio between the amounts of alkali hydroxide and ferric chloride does not change, even if their amount be increased. The titration values indicating the definite ratio between the amounts of alkali hydroxide and ferric chloride are given below.

TABLE I.

KOH ($N/100$).	$FeCl_3$ ($N/100$).	KOH ($N/100$).	$FeCl_3$ ($N/100$).
10. c.c.	9·2 c.c.	60 c.c.	52·0 c.c.
20	17·5	70	59·2
30	26·6	80	68·2
40	35	90	76·9
50	45	100	85·5

The graph representing these values is given in Fig. 1.

Fig. 1.

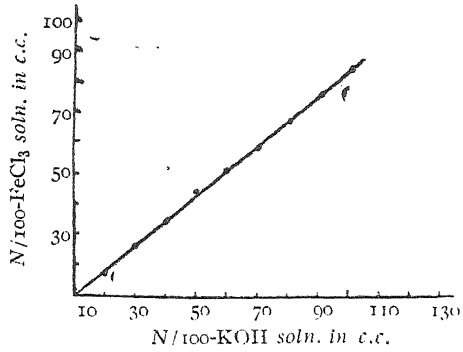
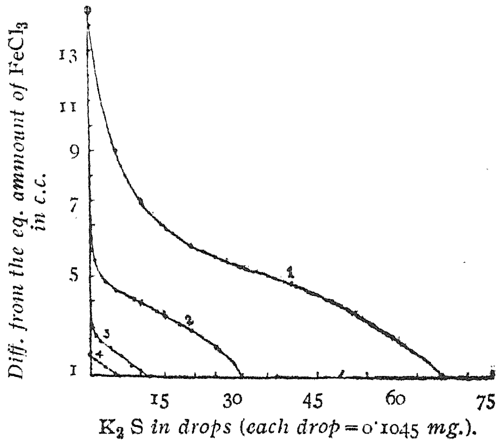


Fig. 2.



Curves 1-4 refer respectively to 100 c.c., 60 c.c., 30 c.c., and 10 c.c.

Table II records the titration values obtained with K_2S showing that definite ratio mentioned is changed progressively by employing a stabiliser. A similar course of change was followed in the cases of other stabilisers.

TABLE II.

1 C.c. of K_2S soln. contains 2·09 mg. ≡ 20 drops. $N/100$-KOH soln. taken = 10 c.c. $FeCl_3$ soln. used = $N/100$.

K_2S (drops). ...	0	1	2	3	4	5	6
$FeCl_3$ required (c.c.) ...	9·20	9·35	9·50	9·65	9·80	9·90	10·00

Fig. 2 shows the course of change found for the different amounts of potassium hydroxide in the case of potassium sulphide. In Fig. 2, the deficit noticed, *i.e.* the difference from the equivalent amount of ferric chloride, has been plotted against the amount of the stabiliser for the different amounts of potassium hydroxide solution employed, namely, 10 c.c., 30 c.c., 60 c.c. and 100 c.c.

Table III records the titration values obtained with K_2S where such stabilising action was not found.

TABLE III.

1 C.c. K_2SO_4 soln. contains 5 mg.$=$20 drops.. 10 C.c. $N/100$ KOH solution taken.

Amount of K_2SO_4 (in drops).	0	1	2	3	4	10
$N/100$-$FeCl_3$ required (c.c.)	9·20	9·15	9·20	9·20	9·20	9·20

To ensure the absence of any stabilising influence, similar titrations were carried out with different amounts of potassium hydroxide solution. Besides potassium sulphate, the substances found to have no stabilising action under these conditions are, sodium succinate and sulphocyanide, ferricyanide, ferrocyanide and indigo-tetrasulphonate of potassium.

Comparative Stabilisation.

The condition of the stability of the sol (as we have inferred) is that the iron salt given by a substance possessed of a stabilising influence, should be a stable one in an alkaline medium. But it may be expected that the negative radicals of these stabilising substances should have an influence on the stabilisation and a comparative study of this influence is feasible following the method of investigation we have adopted. For this purpose an acurate estimation of the amount of the negative radicals in the various substances was made in the following way: Carbonate, citrate, and tartrate radicals were estimated indirectly from an estimation of potassium as potassium sulphate; the sulphide was estimated indirectly from the amount of potassium hydroxide taken for its preparation; the phosphate radical was estimated from ferric phosphate, taking a known amount of ferric chloride; and finally, the silicate was estimated from the amount of silica obtained and also indirectly by removing silica with hydrofluoric and sulphuric acids.

It has been shown that the minimum amount of the stabilising substances, required to bring the ratio between the amounts of alkali hydroxide and ferric chloride to unity, corresponds to a definite stability of the sol produced. Under this condition the amounts of various negative radicals should give an idea of the degree of influence exercised by them. In Table IV the amount of different negative redicals found for the different amounts of potassium hydroxide is given.

TABLE IV.

N/100-KOH sol. *N*/100—$FeCl_3$ soln. used

Radical.	Amount in mgs. corresponding to KOH solution taken in			
	10 c.c.	30 c.c.	60 c.c.	100 c.c.
Citrate	0·3521 mg.	0·7747 mg.	1·4085 mg.	2·8874 mg.
Tartrate	0·4695	1·0955	2·0343	3·2865
PO_4'''	0·3212	0·6424	1·2045	2·7302
SiO_3''	0·3302	0·7338	1·4680	2·642
S''	0·1815	0·3629	0·9073	2·1171
CO_3''	0·7584	1·4220	2·8440	6·3516

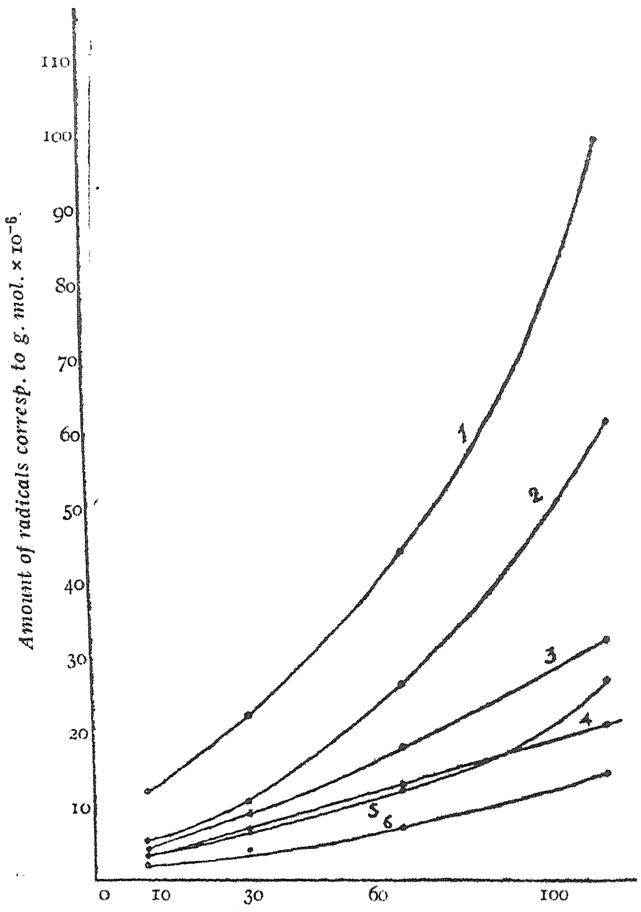
The above figures by themselves convey no idea about the comparative influence. If however they are expressed (*vide* Table V) in terms of gram-ion, an idea of the degree of influence exercised by the radicals becomes apparent.

TABLE V.

Radical.	Amount in g. ions corresponding to the amount of KOH soln. × 10^6 in			
	10 c.c.	30 c..c	60 c.c.	100 c.c.
Citrate	1·862	4·099	7·45	15·28
Tartrate	3·173	7·401	13·74	22·2
PO_4'''	3·382	6·673	12·68	28·74
SiO_3''	4·328	9·618	19·24	34·63
S''	5·662	11·32	28·30	66·04
CO_3''	12·64	23·7	47·4	105·9

The degree of influence exercised follows the order arranged as, citrate > tartrate > phosphate > silicate > sulphide > carbonate. Fig. 3 represents a better manifestation of this comparison. Curves in Fig. 3 show that the amount of the stabiliser, except in the case of the tartrate, is not strictly proportional to the amount of potassium hydroxide taken.

Fig 3.



Curves 1-6 refer respectively to CO_3'', S'', SiO_3'', PO_4''', tartrate and citrate ions.

The stability has also been examined from two other different standards. In one case the time required for coagulation with a $N/100$ solution of lanthanum nitrate, has been noted. This has been done with the sols prepared with double the amount of the stabilising substances, corresponding to the data in Tables VI and VII. The data given below refer to 10 c.c. of the sol in each case. We should mention that a consistent value of the time required for coagulation, is obtained only when the sol is kept rotating since the addition of lanthanum nitrate.

TABLE VI.

	Time required for coagulation with			
$La(NO_3)_3$.	Citrate.	Tartrate.	Phosphate.	Silicate.
10 drops	38 sec.	51 sec.	21 sec	37 sec.
8	49	60	33	25
6	69	75	57	21
4	No coagulation noticed on that day.			19
				70

TABLE VII.

	Time required for coagulation with		
$La(NO_3)_3$.	Sulphide.	Carbonate.	Powis' sol.
10 drops	14·5 sec.	13 sec.	31 sec.
8	18	16	40
6	22	18	51
4	27	25	69
2	35	29·9	142

Data in Tables VI and VIII show that the order of stability mentioned is practically maintained. The sol containing the silicate behaves rather abnormally, the time required for coagulation decreasing at first and then increasing as the amount of lanthanum nitrate is progressively decreased. We may point it out that lanthanum nitrate will give insoluble compounds with the above stabilising substances ; and for this very reason it cannot be an ideal electrolyte for noting coagulation. But a better substitute (having a polyvalent positive radical) will be difficult to obtain. The data given for the sol prepared according to Powis will show that the sol is nearly as stable as the one containing the citrate.

The other standard we have mentioned, is the preservability, *i.e.*, the period till the sol is coagulated if left by itself. We give below the period observed in the different cases.

TABLE VIII.

Stabiliser.	Period.	Stabiliser.	Period.
Silicate	15 days	Citrate	about 5 days
Tartrate	9 to 10 days	Sulphide	6 to 7 hours
Phosphate	5 to 6 days	Carbonate	4 to 5 hours
		Powis' sol.	about 4 days

We shall find that in respect of spontaneous coagulation, the previous order has not been maintained. We have also seen that the sol prepared with citrate, can be preserved for a longer period in winter than in summer.

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On the Physico-Chemical Properties of Electrodialysed Gels of Silica, Alumina, Ferric Hydroxide and their Mixture. Part I. Ion Exchange.

By Promode Behari Bhattacharyya and Kalipada Ganguli.

Recent investigations carried out in this laboratory showed that the clay fraction in laterite soils exceed 40%. Their agricultural properties, however, do not at all correspond to those of heavy soils. Of the various investigations concerning the silica sesquioxide ratio, reference should be made to those of Mattson (First International Congress of Soil Science, Vol. 2, p. 199) on the adsorption of cations and anions by soil colloidal materials and to those of Ghosh and Bhattacharyya (*Soil Science*, 1930, **29**, 311) on the adsorption of calcium and phosphate ions, as those investigations have a bearing on the present one.

Anderson (*J. Agric. Res.*, 1929, **38**, 565) has recently studied the influence of substitution of cations on the various physical properties with varying $SiO_2/Al_2O_3 + F_2O_3$ ratios of the soil colloids. The relation between the experimental results of these investigators and those of ours will be discussed later. As stated in a previous publication (Ghosh and Bhattacharya, *loc. cit.*) mixed gels of silica + alumina and silica + ferric oxide as obtained by mutual precipitation may have properties comparable resulting in some respects those of the soil colloids.

EXPERIMENTAL.

Silica Gel.—It was prepared by hydrolysing pure silicon tetrachloride in a large volume of water and then adding an excess of ammonia. The gel obtained was then electrodialysed in a 220 volt current for a long time with a constant flow of conductivity water until there was no trace of ammonia and chlorine in the cathode and anode respectively. The presence of ammonia was tested with the help of Nessler's reagent and that of chlorine determined electrometrically (Bell and Doisy, *J. Biol. Chem.*, 1920, **44**, 45). The electrodialysed gel was then filtered and dried in an electric oven kept at a constant temperature of 34° until the weight of the dry gel was found constant.

Aluminium Hydroxide Gel.—Ammonia was added in excess to a solution of pure aluminium chloride in water. The gel of aluminium hydroxide was then electrodialysed in exactly the same way as before until there was no trace of chlorine and ammonia. The electrodialysed gel after filtration was dried as before.

Ferric Hydroxide Gel.—Excess of ammonia was added to a solution of pure ferric chloride in water. The jelly-like mass so obtained was electrodialysed, filtered and dried to constant weight as in the previous cases.

Preparation of mixed Gels of (a) Silica and Aluminium hydroxide, (b) Silica and Ferric hydroxide by Mutual Precipitation.—$SiCl_4$ was hydrolysed in a large volume of water containing $AlCl_3$ or ferric chloride in solution, and then excess of ammonia was added to obtain a precipitate of both in presence of each other. The jelly-like mass was then electrodialysed, filtered and dried to constant weight as before.

The percentage of SiO_2 and Al_2O_3 in the ignited sample was estimated.

TABLE I.

Mixture No.	Composition.		Ratio.
I	SiO_2, 72%	Al_2O_3, 28%	$SiO_2/Al_2O_3=4\cdot37$
II	,, 44	,, 56	,, $=1\cdot33$
III	,, 58	Fe_2O_3, 42	$SiO_2/Fe_2O_3=3\cdot68$
IV	,, 28	,, 72	,, $=1\cdot04$

Saturation of Samples prepared with NaCl, KCl, $CaCl_2$ *and* $MgCl_2$.—Normal solutions of NaCl, KCl, and $MgCl_2$ were first prepared.

Four stoppered conical flasks, each containing about 5 gms. of Fe_2O_3 were shaken with 50 c. c. of normal solution of NaCl, KCl, $CaCl_2$ and $MgCl_2$ in a shaking machine for about 8 hours. The suspensions in different electrolytes were then kept over-night. After removing the supernatant liquids, 50 c. c. solutions of normal NaCl, KCl, $MgCl_2$, $CaCl_2$ were again introduced into the flasks as before and shaken again for about 6 hours.

The suspensions were then filtered and washed with water until the concentration of chlorine ion in the filtrate was 1×10^{-5} chlorine or less. The concentration of chlorine ion was tested electrometrically (*cf.* Bert, *J. Agric. Sci.*, 1929, **91**, 533).

Other gel samples were also treated exactly in the same way as this one.

The samples were dried to constant weight at 34°; moisture present in the samples was determined in each case and was taken into reconsidration in calculating the amount of ions adsorbed.

Estimation of Na, K, Ca, Mg *in the Saturated Samples.*

Each of the saturated substances was extracted with N-NH_4Cl. Sodium was estimated in the extracted solution gravimetrically by the magnesium uranyl acetate method as recommended by Kahane (*Bull. Soc. chim. France*, 1930, **47-48**, 4).

Potassium was estimated colorimetrically by precipitating it as potassium chloroplatinate (Hill, *J. Amer. Chem. Soc.*, 1903, **25**, 990).

Calcium was precipitated as Ca-oxalate and titrated with $N/100$ $KMnO_4$. An improvement in the technique was introduced by using frittered jena-glass filter and filtrating directly the precipitate adhering to the filter after washing with permanganate.

Magnesium was estimated colorimetrically. It was separated as magnesium ammonium phosphate and the latter converted into phosphomolybdate which in turn was treated with the hydroquinone and carbonate-sulphite solution of Bell and Doisy (*J. Biol. Chem.*, 1920, **44**, 55) and the resulting colour matched against a standard.

Blank estimations of Na, K, Ca, and Mg in very dilute solutions of their chloride gave the following limits of error :—Na, $\pm 2{\cdot}5$ %; K + Mg, ± 5 %; Ca, ± 3 %.

A portion of the saturated samples was shaken with an excess of a saturated solution of magnesium nitrate for about 6 hours, filtered and washed several times with saturated magnesium nitrate solution. Chlorine was then estimated electrometrically (Bert, *loc. cit.*) in the filtrate. Absolutely pure magnesium nitrate was used in all these cases.

In calculating amount of adsorption, the water of hydration was taken into consideration. In our experiments the materials after saturation with the different salt solutions were washed until the Cl′-ion concentration was less than 1×10^{-5}. The gels in the wet state never contained more than 66% water; on this basis the Cl′-ion in the water of hydration per gram of dried gel comes to about 2×10^{-8}. From the data it will be observed that this amount is negligibly small compared with the amount of Cl′-ion found by exchange from the different gels. Also the amount of cations as obtained by exchange is of the order of 1×10^{-4}. Thus the amount of positive and negative ions in the water of hydration do not appreciably affect our results.

Experimental results are given in Tables II to VI.

TABLE IIa.

Exchangeable cations.

Saturated with.	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.
	SiO_2		Al_2O_3		Fe_2O_3	
NaCl	0·28	16·86	0·23	23·94	0·05	8·61
KCl	0·09	5·58	0·09	8·99	0·07	11·18
$CaCl_2$	0·11	7·02	0·07	7·18	0·12	19·29
$MgCl_2$	0·21	12·86	0·05	4·94	0·10	16·27

TABLE IIb.

Samples used (1 g.) are same as in Table I.

Saturated with.	M. equiv./g. of the substance.	* Exchangeable cations.	M. equiv./g. of the substance.	* Exchangeable cations	M. equiv./g. of the substance.	* Exchangeable cations.	M. equiv./g. of the substance.	* Exchangeable cations.
	Mixture (I)		Mixture (II)		Mixture (III)		Mixture (IV)	
NaCl	0·482	0·27	0·27	0·25	0·271	0·18	0·31	0·12
KCl	0·28	0·09	0·13	0·09	0·19	0·08	0·13	0·08
$CaCl_2$	0·15	0·10	0·15	0·09	0·25	0·11	0·13	0·12
$MgCl_2$	0·33	0·17	0·31	0·12	0·23	0·16	0·49	0·13

* Calculated from the law of addititive mixtures given in m. equiv. per g. of the substance.

TABLE IIIa.

Exchangeable Cl′-ion.

Saturated with.	SiO$_2$		Al$_2$O$_3$		Fe$_2$O$_3$	
	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.	M. equiv./g. of the substance.	M. equiv./g. mol. of the substance.
NaCl	Nil	Nil	0·06	6·18	0·02	3·43
KCl	,,	,,	0·06	6·18	0·02	3·43
CaCl$_2$	,,	,,	0·06	6·18	0·035	5·62
MgCl$_2$	,,	,,	0·06	6·18	0·034	5·44

TABLE IIIb.

Samples used are same as in Table I.

Saturated with.	Mixture (I)		Mixture (II)		Mixture (III).		Mixture (IV)	
	M. equiv./g. of the substance.	*Calc. value of anion exchangeable.	M. equiv./g. of the substance.	*Calc. value of anion exchangeable.	M. equiv./g of the substance.	*Calc. value of anion exchangeable.	M. equiv./g. of the substance.	*Calc. value of anion exchangeable.
NaCl	0·0030	1·09	0·018	3·30	0·0059	2·25	0·024	5·32
KCl	0·0029	1·06	0·010	2·00	0·0050	1·90	0·020	4·44
CaCl$_2$	0·0028	1·02	0·013	2·34	0·0063	2·40	0·017	3·82
MgCl$_2$	0·0028	1·02	0·013	2·40	0·0055	2·10	0·023	5·05

* Value of anion exchangeable per g. mol. of sesquioxide, taking the sesquixide as the only adsorbing material.

TABLE IV.**

Silica powder.

3·3087 gms. of the powder was suspended in 250 c.c. water (Sp. C. $1·5 \times 10^{-6}$ at 30°).

*p*H of suspension = 5·6 (by Folien colorimeter)
= 5·5 (by quinhydrone electrode)
Sp. C. of suspension at 31·5° = $1·88 \times 10^{-5}$ mhos.
*p*H of supernatant liquid = 6·0 (by Folien colorimeter)
= 6·1 (by quinhydrone electrode).
Sp. C. of supernatant liquid at 31° = $1·88 \times 10^{-5}$ mhos.

TABLE V.**

Suspended silica gel.

Dilution.	*p*H by quinhydrone.	*p*H by colorimeter.	Sp. conducty. × 10^5.
Pure	4·91	4·8–5·0	4·489
5 times	5·80	5·6–5·8	1·825
10	5·87	5·6–5·8	1·169
20	6·08	5·8–6·0	0·956

TABLE VI.**

Supernatant liquid of silica gel.

Dilution.	*p*H by quinhydrone.	*p*H by colorimeter.	Sp. conducty × 10^5.
Pure	5·41	5·2–5·4	4·489
5 times	6·00	5·8–6·0	1·500
10	6·10	6·0–6·2	1·096
20	6·10	6·0–6·2	0·742

DISCUSSION.

A portion of the silica gel purified by electrodialysis was kept in a flask. This was analysed after the experiments were finished (after 2 years) under the supervision of Prof. J. N. Mukherjee. The results will give an idea as to the purity of the gel prepared by us. This is of importance because the properties of colloidal precipitates are often dependent on the degree of purity as also on the method of precipitation.

In Tables IV, V and VI are given the *p*H and conductivity of silica powder, suspended silica gel and the supernatant liquid of the gel. As pointed out by Mukherjee, "The silica contained electrolytes which increased the specific conductivity of water from $1·6 \times 10^{-6}$ to $4·5 \times 10^{-5}$." When a chloride is titrated with an $AgNO_3$ solution, at the theoretical end-point the Cl-ion concentration becomes of the order of 1×10^{-5}." Electrodialysis was stopped when the Cl′-ion concentration in the gel and in the dialysate was of this order. Our gel, therefore,

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** *p*H of conductivity water = 6·5 (by B.T.B.). Sp. conductivity of water = $1·6 \times 10^{-6}$. Measurements carried out at room temperature (31°–32°).

Our best thanks are due to Mr. B. R. Mazumdar, M.Sc. for these determinations of Sp. conductivity and *p*H values.

contained, after electrodialysis, the colloidal ions and gegenions and a small quantity of electrolyte, HCl, as is evident from its conductivity.

The possible anions on the surface of the silica gel are the hydroxyl and silicate ions. Structurally it may be represented as follows :—

$$\begin{array}{l|l} x\,(SiO_2 + yH_2O) & \\ z\ \ HSiO_3^- & z\ H^+ \\ n\ \ OH^- & n\ H^+ \end{array}$$

The cations on the liquid side are only the equivalent amount of H^+ ions. Again on the surface of alumina and ferric hydroxide gels, there may be $Al(OH)_2'$, $Al(OH)''$ and Al''' ions and $Fe(OH)_2'$, $Fe(OH)''$ and Fe''' ions respectively, and also hydrogen ions. On the liquid side there are hydroxyl ions. Structurally :—

$$\begin{array}{ll|l} x\ \ [Al(OH)_3+yH_2O], & m\ Al(OH)_2^+ & m(OH)^- \\ & n\ Al(OH)^{++} & n\ 2(OH)^- \\ & p\ Al^{+++} & p\ 3(OH)^- \\ & q\ H^+ & q(OH)^- \end{array}$$

When excess of salt solution comes in contact with the silica gel the main possibilities are :—Primary adsorption of the anions of the salt on the surface, adsorption of equivalent amount of cations of the salt by electrical attraction, exchange of cations on the liquid side of the gel with those of the salt. Such adsorption and exchange process might also occur in case of alumina and ferric hydroxide; had exchange adsorption been the only process occurring, one would expect the adsorption of cations of the salt on the surface of silica gel and displacement of equivalent amount of H^+ ions out of the double layer into the liquid.

Besides ion-exchange and ion-adsorption, contact with neutral salt solution may change the structure of the electrodialysed gel. We have noted that during the process of electrodialysis, the gels are flocculated and form a stiff mass on the anode side of the middle chamber. This material can be redispersed by vigorous shaking. The nature of the gel is determined mainly by the cations in the outside layer. According to the Wiegner "If the cations present in soils are more highly hydrated as sodium and magnesium ions, the soil becomes converted into a dense impervious mass which on suspension in water subsides very slowly *i.e.*, coagulates with difficulty; but the more slightly hydrated ions the soil contains, as for instance potassium and calcium ions, the greater is its degree of coagulation."

In our experiments, the electrodialysed gels were first saturated with the chlorides of Na, K, Ca and Mg respectively, and the effect of leaching with pure water until the wash-liquid was free from Cl′-ion was studied. The cations retained by these well-washed gels were determined by ammonium chloride extraction as recommended by Mattson (*J. Agric. Sci.*, 1926, **33**, 553) who showed that this process removed quantitatively the whole of the exchangeable bases and that the same amount was exchangeable by electrodialysis. Bradfield (*First Int. Congress, Soil Sci.*, 1928, **2**, 264) has also confirmed this view. Hence we can assume that all bases exchangeable under the condition of our experiment were removed by the NH_4Cl extraction. Again absorbability of anions has been shown by Mukherjee (*J. Indian Chem. Soc.*, 1924, **1**, 173) to be in the order $NO_3 > I > SO_4 > Cl$. So the $Mg(NO_3)_2$ extraction in our experiments is expected to give all the exchangeable chlorine ions.

It will be observed from Tables II and III that there is no stoichiometric relationship between the exchangeable metal ions and chlorine ions. Silica yields by exchange considerable amount of cations but no Cl′-ions. Probably it does not adsorb any Cl′-ions which is due to the fact that "Silica has a strong capacity to absorb OH ions and to a much less extent other anions" and that in presence of water, the surface is saturated with OH ions.

Exchangeable Cl′ ions per g. of alumina, as shown in Table III, is approximately the same and is independent of the metal ion which formed the chloride. Adsorption of Cl′-ions is mainly due to the replacement of OH ions (as was evident from a rise in p_H of the washed liquid). The same also applies in the case of ferric oxide gel, where the exchangeable Cl′ ion of the Na-saturated material is the same as that of the K-saturated material. Also the Ca and Mg-complexes again yield equivalent amounts of exchangeable Cl′ ions.

In the case of each of the silica sesquioxide mixtures the same amount of chlorine ions (shown in Table III) is obtained independent of the metal chloride used for exchange. Since silica does not adsorb Cl, this anion is evidently obtained from the sesquioxides present in the mixtures. This confirms the suggestion of Mattson (*loc. cit.*) that the adsorption of anions by soils is due to the presence of free sesquioxides in the soils. The data clearly show that the exchangeable quantities of anions increase with a decrease in the ratio of silica to sesquioxide as has been shown by Mattson for a wide range of soils. Columns (3, 5, 7 and 9) of Table III*b* give the exchangeable Cl′-ions per g. mol. taking sesquioxides as the active adsorbing material. Pure alumina yields much larger amount of exchangeable chlorine ion than an equivalent of alumina in a silicate mixture. This shows that the presence of silica in the mixture has diminished the active adsorbing surface of alumina. This also holds good for the SiO_2/Fe_2O_3 mixtures. Fig. 2 *a*, *b* show the effect of silica on the amount of Cl′-ions obtained by exchange from alumina and ferric hydroxide, when present in different proportions. In the case of SiO_2/Fe_2O_3 mixture IV, however, Na- and K-saturated samples yield larger amounts of Cl′ ions than the Na- and K-saturated pure ferric hydroxide gel. Hence, silica at low percentage tends to increase the active adsorbing surface of the Na- and K-saturated ferric hydroxide gel. An explanation of such a peculiar behaviour has recently been put forward by Mattson (*Soil Sci.*, 1935, **39**, 161).

It is found that in pure alumina, the exchangeable amount of cations is in the order Na > K > Ca > Mg. In ferric hydroxide, however, the milli-equivalents of Ca and Mg are almost the same and are practically double the milliequivalents of sodium or potassium per gram of the gel; we may therefore infer that for 1 g. of the material there is a definite number of points on the surface to which an exchangeable ion of Ca, Mg, Na or K can get fixed.

FIG. 1(*a*).

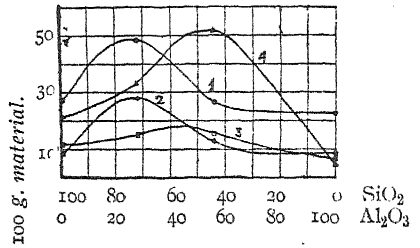


FIG. 1(*b*).

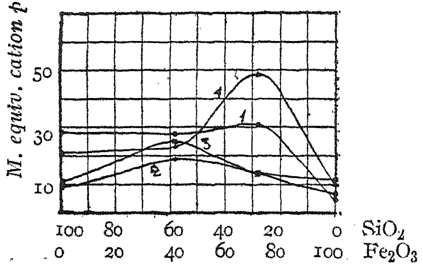


FIG. 2(*a*).

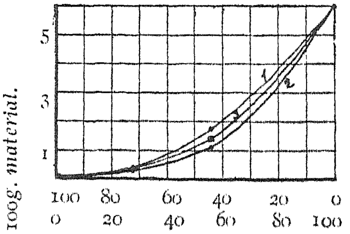
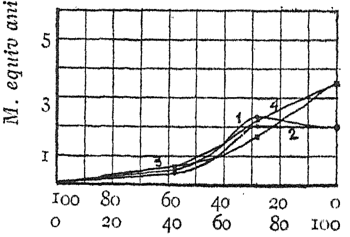


FIG. 2(*b*).



Gel composition.

Curves 1-4 refer respectively to Na, K, Ca and Mg saturated materials.

Cation exchange in case of silica sesquioxide gels is always greater than that calculated from the law of mixture, the maximum difference being observed in the case of magnesium saturated gel. This shows that exchange of bases in soils is mainly regulated by the presence of silica. As a matter of fact the amount of exchangeable Na in one g. of pure silica gel is the same as that in 1 g. of silica-alumina mixed gel containing only 0·44 g. of silica. It is also remarkable that whereas the amount of exchangeable metal ion from pure ferric hydroxide is small compared with silica, mixed gels of ferric oxide and silica yield more metal ions than pure silica itself. This indicates a great increase in the degree of dispersion of silica gel when precipitated with ferric hydroxide. Such is also the case with SiO_2/Al_2O_3 mixtures. Fig. 1*a* and *b* show the relation between the composition of gels and exchangeable cation. It may be noted here that the amounts of exchangeable ions in these artificial gels are of the same order of magnitude as are noticed in the clay fractions of soils.

Our best thanks are due to Prof. J. C. Ghosh for suggesting this work and his continued interest and advice.

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A Note on the Constitution of the Reduction Product of Trichloromethylparaconic Acid.

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The reduction of trichloromethylparaconic acid (I) has been studied by Fittig and Miller (*Ber.*, 1887, **20**, 3181; *Annalen*, 1889, **255**, 43) and Meyers (*J. Amer. Chem. Soc.*, 1902, **24**, 525). They assign the formula (II) to the reduction product.

While studying the condensation of chloral with various acids, the present authors had occasion to prepare trichloromethylparaconic acid and reduce it. As a result of their work they consider the reduction product is a dibasic acid as represented in formula (III) and has not the structure (II) given by Fittig and Miller. This has been proved (*a*) by preparing from the reduction product diesters (IV and IVa), anhydride (V), diacid chloride (VI), dianilide (VII) and di-*p*-toluidide (VIII), (*b*) by reducing the ethyl ester (IX) and anilide (X) of trichloroparaconic acid to produce respectively the acid ester (XI) and acid anilide (XII) which give the diester (IV) and dianilide (VII), and (*c*) by preparing tricarballyic acid (XIII) by the action of concentrated sulphuric acid which converts the CH_2CHCl_2 group to CH_2COOH group (Meldrum and Vaidyanathan, *Proc. Indian Acad. Sci.*, 1935, **1**, 510).

EXPERIMENTAL.

Butane-δ δ-dichloro-αβ dicarboxylic acid (III), the reduction product under discussion, was prepared according to Fittig and Miller (*loc. cit.*), (Found: Equiv., 107·6. Calc. for dibasic acid, 107·5).

The methyl ester (IVa) is a colourless oil. b. p. 135°/11 mm. (Found : Cl, 29·0. $C_8H_{12}O_4Cl_2$ requires Cl, 29·2 per cent).

The ethyl ester (IV) is a sweet smelling oil, b.p. 215°/50 mm. (Found: Cl, 26·7. $C_{10}H_{16}O_4Cl_2$ requires Cl, 26·9 per cent).

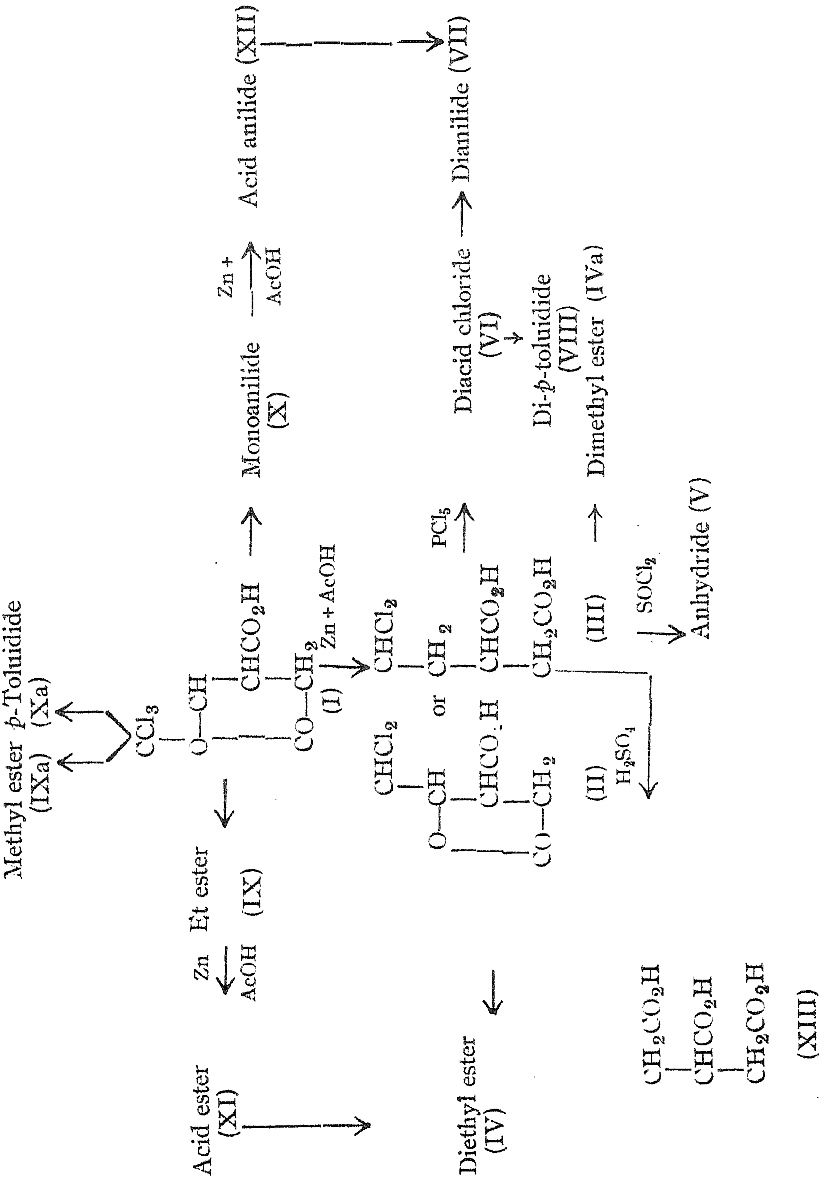
The annydride (V).—The product (III)(5g.) was treated with thionyl chloride (7g.) at 65° for 4 hours and the excess of thionyl chloride was removed at 95°. The residue after being dried on a porous plate was crystallised from petroleum ether in shining plates, m.p. 76°-77°. (Found: Cl, 36·1. $C_6H_6O_3Cl_2$ requires Cl, 36·0 per cent).

The crude acid chloride (VI) was obtained by heating the reduction product (5 g.) with PCl_5 (10 g.) and after cooling pouring into petroleum ether, the precipitated anhydride was removed and the residue distilled, b.p. 123°/5 mm.

The anilide (VII), obtained from the acid chloride (VI) in petrol ether, crystallised from dilute acetic acid in needles, m.p. 176°-77°. (Found: Cl, 19·4. $C_{18}H_{18}O_2N_2Cl_2$ requires Cl, 19·7 per cent).

The p-*toluidide* (VIII) crystallised from dilute acetic acid, m.p. 209°-10°. (Found: Cl, 18·0. $C_{20}H_{22}O_2N_2Cl_2$ requires Cl, 18·0 per cent).

Tricarballylic acid (XIII).—The reduction product (III) (10g.) was treated with concentrated sulphuric acid (20 c.c., 95 %) at 100° for 3 hours and the liquid poured on ice and neutralised with lead carbonate. The filtrate was twice extracted with ether to remove unchanged reduction product and the aqueous solution concentrated, filtered and cooled. The resulting precipitate was crystallised from hot water, m.p. 165°,


Methyl ester (IXa)
p-Toluidide (Xa)
CCl3
O—CH
CO—CH2
CHCO2H
(I)
Et ester (IX)
Zn AcOH
Acid ester (XI)
Monoanilide (X)
Zn + AcOH
Acid anilide (XII)
Dianilide (VII)
Zn + AcOH
CHCl2
O—CH
CHCO2H
CO—CH2
(II)
or
CHCl2
CH2
CHCO2H
CH2CO2H
(III)
PCl5
Diacid chloride (VI)
Di-p-toluidide (VIII)
Dimethyl ester (IVa)
Diethyl ester (IV)
H2SO4
SOCl2
Anhydride (V)
CH2CO2H
CHCO2H
CH2CO2H
(XIII)

(recorded 165°). The *anhydride* melts at 132°-34° (recorded 132°) and the *anilide* melts at 262°-64° (recorded 252°).

Derivatives of Trichloromethylparaconic acid (I).

The methyl ester (IXa) crystallised from methyl alcohol, m.p. 77°. (Found: Cl, 40·7. $C_7H_7O_4Cl_3$ requires Cl, 40·7 per cent).

The ethyl ester (IX) is a colourless sweet smelling oil, b.p. 173°/10 mm. (Found: Cl, 38·5. $C_8H_9O_4Cl_3$ requires Cl, 38·6 per cent).

The anilide (X) crystallised from dilute acetic acid in light shining plates, m.p. 165°-66°. (Found: Cl, 32·7. $C_{12}H_{10}O_3NCl_3$ requires Cl, 33·0 per cent).

The p-*toluidide* (Xa) crystallised from dilute alcohol in thin white plates, m.p. 173°-74°. (Found: Cl, 31·8. $C_{13}H_{12}O_3N\ Cl_3$ requires Cl, 31·6 per cent).

The ethyl hydrogen ester (XI).—(IX) was reduced with zinc and acetic acid as usual, b.p. 190°/20 mm. (Found: Cl, 29·0. $C_8H_{12}O_4Cl_2$ requires Cl, 29·2 per cent).

The acid anilide (XII), obtained by the reduction of (X) with zinc and acetic acid, crystallised from chloroform, m.p. 121°-22°. (Found: Cl, 24·7. Equiv., 289·2. $C_{12}H_{13}O_3NCl_2$ requires Cl, 24·4 per cent. Equiv., 290·1).

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'Thermo-ageing' of Colloids. Part I. Variation of Refractivity.

By Shridhar Sarvottam Joshi and P. V. Jagannatha Rao.

Work of a number of investigators would appear to show that a freshly prepared colloid does not represent an equilibrium condition between the micelles and the dispersion medium. Usually, the viscosity and the flocculation value, for example, in the case of fresh sols diminish and become stationary on allowing to stand. The corresponding viscosity (that is, after allowing to stand) and in numerous cases, the conductivity vary in the opposite sense. Surface tension also changes, though not always in the same direction. These are the principal facts observed during the 'ageing' of colloids. The interesting work of Davies (*J. Phys. Chem.*, 1929, **33**, 274) indicates that temperature might be an important factor in this process. It is extremely likely that the nature and the size of the particles change presumably comparably to what is produced in coagulations. In the results published elsewhere in this Journal, it has been found that μ, the refractive index of a colloid, changes sensibly during coagulation. Corresponding data, distinctive of the influence of 'ageing' on μ, are not available in the literature of the subject. The scope of the following experiments has been restricted to changes in μ due to 'thermo-ageing', that is, when the colloid was allowed to stand at moderately high temperatures for definite periods. Corresponding results for 'ageing' at ordinary temperatures, now in the course of compilation in these laboratories, will be communicated shortly.

Experimental.

Colloidal solutions of arsenious and antimony sulphides (Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, **8**, 11, 337), manganese dioxide and ferric oxide (Joshi and Lal, *ibid.*, 1933, **10**, 61; Joshi and Nanjappa, *ibid.*, 1933, **10**, 599) were prepared and their colloid contents estimated as described previously (*loc. cit.*) in this series.

Cadmium sulphide sol was prepared by adding drop by drop concentrated ammonia to a 10 per cent. solution of cadmium sulphate, until the precipitate produced just dissolved. On saturating this with hydrogen sulphide, a heavy precipitate and a yellow supernatant solution were obtained, which were allowed to stand overnight. The clear solution was then decanted off and the excess of hydrogen sulphide expelled by prolonged warming. The sol was then stocked in a well cleaned jena bottle, and its colloid content estimated by evaporating to dryness a suitable known volume of the sol and weighing the residue accurately.

Colloid sulphur was prepared by mixing carefully saturated solutions of hydrogen sulphide and sulphur dioxide. The excess of either of the dissolved gases was first driven out by gentle warming; the process was completed by leading a current of pure hydrogen through the colloid. Its content was estimated as in the case of colloid cadmium sulphide. Mercury sulphide sol was obtained from aqueous mercury cyanide by a method similar to that followed with colloid arsenious sulphide. Its colloid content was estimated approximately as in the last case·

Cupric oxide sol was prepared by Bredig's method with some modifications. Two stout rods of pure copper were used as electrodes, and the colloid obtained by intermittent sparking. A regularity in the frequency of this process, which was found essential in giving a stable sol with a uniform dispersion of the colloid material, was secured by mounting one of the electrodes on a firm and flexible support which vibrated by contact with the axle of a motor kept running at a uniform speed. The voltage between the electrodes was about 70 and the current about 4 amps. A very considerable amount of heat was produced, which had an instabilising action on the colloid. This was reduced to a minimum by cooling with a rapid stream of water. The colloid content was estimated by the iodometric estimation of copper in a known amount of the sol.

The aluminium hydroxide sol was prepared by the hydrolysis of a dilute solution of aluminium acetate and subsequent removal of acetic acid by careful heating as recommended by Crum (*Annalen*, 1854, **89**, 156). The colloid content was obtained by the gravimetric estimation of aluminium trioxide from a known amount of the sol when treated with dilute ammonia.

Colloid thorium hydroxide was prepared by first forming a suspension of the hydroxide by treating aqueous thorium nitrate with an excess of ammonia. This was then heated nearly to the boiling point, and maintained in this condition for about seven hours with intermittent additions of small quantities of dilute hydrochloric acid. The resulting fine opalescent sol was then purified by dialysis.

The vanadic acid sol was prepared by first making a paste of a finely powdered sample of the acid with distilled water. It was then taken up with more water in successive small additions and finally filtered through a double filter paper. The colloid content was estimated as in the case of the sulphur sol.

In preparing the copper ferrocyanide sol, solutions of about 1% copper sulphate and about 0·1 % potassium ferrocyanide were mixed carefully. The resulting sol which was of a clear brown colour showed incipient coagulation after about a couple of days on standing. The refractive index measurements were, therefore, made with a fresh sample. It contained traces of potassium sulphate as an electrolytic impurity produced during the colloid formation. The colloid content was estimated after first removing the cyanide, acidifying with acetic acid and estimating the copper present iodometrically.

To a cold and freshly prepared solution of about 0·2 g of potassium ferrocyanide in 200 c.c. of water, small amounts from a solution of 0·04 g. of ferric chloride in 200 c.c. water were added with continuous stirring. The resulting sol of Prussian blue was found to be stable for at least two months. Its colloid content was estimated by an iodometric determination of its iron content as described in the previous case.

Colloid selenium was prepared by reducing with a current of sulphur dioxide, a solution containing about 0·25 g. of selenium dioxide dissolved in about 200 c.c. of warm water. The excess of sulphur dioxide was driven out completely by a careful and prolonged warming. The strength of the sol was obtained by the coagulation of a known volume of the sol.

Zsigmondy's method (*cf.* Von Weimarn, *Kolloid Z.*, 1923, **33,** 81) was used for preparing colloidal silver. *N*/200-solution of silver nitrate was warmed gently with the requisite proportion of alkaline formaldehyde in dark. In estimating the colloid content, a known amount of sol is taken and dissolved by addition of concentrated nitric acid. To this was then added dilute hydrochloric acid, which precipitated silver chloride. This was filtered, washed, dried, weighed, and the corresponding amount of silver suspended in the sol calculated. Essentially the same method was used in preparing the gold sol from gold chloride. A clear and a very stable red sol was obtained. The colloid content was estimated approximately by a gravimetric estimation of metallic gold from a known amount of the colloid.

Colloid silver chloride was prepared by adding very slowly and carefully from $N/100$-potassium chloride solution to $N/100$-silver nitrate. The resulting sol was then dialysed for about 72 hours until free from the electrolytes. The colloid was stocked in a jena container and screened from light throughout the work. The colloid content was estimated by a gravimetric estimation of silver chloride by coagulating a known amount of the sol.

The *til* and fish oil (μ_D=1·4650, 1·4802, respectively at 30°) emulsions were prepared by the precipitation method (*cf.* Joshi, *Kolloid Z.*, 1923, **34**, 197). About one c. c. of each of these oils was dissolved in a few c. c. of absolute alcohol. This was then poured in about a litre of twice distilled water which was kept boiling hot, and the mixture vigorously shaken. Excess of alcohol was removed by boiling off carefully. The emulsion was then filtered using a double filter paper of close texture and was found to be quite stable.

The refractive index measurements were first made at 30° with a Pulfrich refractometer in a manner and with precautions as described elsewhere in this Journal (1936, **13**, 141). A definite volume of the colloid was then 'thermo-aged' by boiling slowly and carefully under reflux condenser for 2½ hours on a free flame in the majority of cases. It was then allowed to cool. The loss by evaporation of water during this period was found to be only about 0·5 c. c., which was made up by adding the necessary amount of water. It was observed, in the case of arsenious sulphide, cupric oxide, silver, silver chloride and the oil suspensiods, that the boiling had a flocculating effect. In these cases the sols were 'thermo-aged' by merely heating on a water-bath for the above period. Refractive index in all the cases was redetermined at 30°. Every observation was repeated at least twice using different samples of the colloid and fully reproducible results were obtained. The concentration of the colloid was varied at least by half in every case. These results are given in the tables.

TABLE I.

Colloid.	Colloid content.	μ_1 before heating.	μ_2 after heating.	Change in μ.
Mercuric sulphide	0·3 g./litre	1·33214	1·33221	0·00007
	0·2	1·33214	1·33221	0·00007
Antimony sulphide	2·1	1·33214	1·33221	0·00007
	1·05	1·33206	1·33214	0·00008

TABLE I (contd.).

Colloid.	Colloid content.	μ_1 before heating.	μ_2 after heating.	Change in μ.
Arsenious sulphide	6·6 g./litre.	1·33487	1·33495	0·00008
	1·8	1·33260	1·33268	0·00008
Cadmium sulphide	2·2	1·33206	1·33214	0·00008
	1·1	1·33206	1·33214	0·00008
Sulphur hydrosol	0·15	1·33175	1·33183	0·00008
Manganese dioxide	2·50	1·33214	1·33221	0·00007
	1·25	1·33214	1·33221	0·00007
Cupric oxide	0·85	1·33260	1·33268	0·00008
	0·30	1·33198	1·33206	0·00008
Ferric hydroxide	1·2	1·33268	1·33276	0·00008
	0·9	1·33268	1·33276	0·00008
Aluminium hydroxide	1·2	1·33299	1·33307	0·00008
	0·8	1·33291	1·33299	0·00008
	0·3	1·33284	1·33299	0·00015
Thorium hydroxide	5	1·33206	1·33214	0·00008
	2·5	1·33198	1·33214	0·00016
	1·25	1·33191	1·33206	0·00015
Vanadic acid	1·1	1·33214	1·33221	0·00007
	0·5	1·33206	1·33214	0·00008
	0·37	1·33206	1·33214	0·00008
Prussian blue	3·0 (as Fe)	1·33487	1·33495	0·00008
	0·6 (as Fe)	1·33291	1·33299	0·00008
Copper ferrocyanide	0·4 (as Cu)	1·33260	1·33268	0·00008
	0·2 (as Cu)	1·33260	1·33268	0·00008
Selenium	0·8	1·33214	1·33221	0·00007
	0·6	1·33214	1·43221	0·00007
Silver hydrosol	0·3	1·33206	1·33214	0·00008
	0·15	1·33198	1·33206	0·00008
Gold hydrosol		1·33214	1·33221	0·00007
		1·33206	1·44214	0·00008
Silver chloride	1·25	1·33260	1·33268	0·00008
	1·0	1·33253	1·33260	0·00007
	0·75	1·33245	1·33253	0·00008
	0·5	1·33328	1·33253	0·00015
Til oil emulsion	C	1·33184	1·33191	0·00007
	C/2	1·33184	1·33191	0·00007
Fish oil emulsion	C_1	1·33198	1·33206	0·00008
	$C_1/2$	1·33198	1·33206	0·00008

DISCUSSION.

Since sols were 'thermo-aged' by boiling, except when this produced a sensible instabilisation of the colloid, it would appear that at least two factors are involved, *viz.*, (*i*) a pure temperature effect, which is probably mainly fundamental to 'thermo-ageing' and (*ii*) accessory mechanical effects such as the breaking of the air-liquid interface, convection currents, etc., attendant upon ebullition. On the whole, these latter would appear to be analogous to the possible influence of shaking, stirring etc., on the coagulation of colloids (Smoluchowski, *Z. physikal. Chem.*, 1917, **92**, 155, *et al*; Freundlich and Basu, *ibid.*, 1925, **118**, 203; Freundlich and Kroch, *ibid.*, 1928, **129**, 368; Freundlich, 'Colloid and Capillary Chemistry,' 1926, p. 439; Joshi and Narayan, *J. Indian Chem. Soc. Ray Comm. Vol.*, 1933, pp. 41—52; Joshi and Iyengar, *J. Indian Chem. Soc.*, 1934, **11**, 573). On general grounds, one would anticipate that stirring would accelerate coagulation, presumably chiefly by increasing the frequency of micellar collisions. A review of the literature (*vide supra*) shows, however, that this anticipation is not alwaws realised in practice. Works of Freundlich and co-workers (*loc. cit.*) and of Joshi and Iyengar (*loc. cit.*) show that the accelerating influence of stirring obtains only when it is vigorous and *at moderate and higher concentrations of coagulating electrolytes.* As regards these effects in the absence of any coagulating electrolytes, no data appear to exist in the literature.

The foregoing results show that in every one of the 42 cases of the nineteen sols examined, μ, the refractive index of the colloid is increased sensibly as a result of 'thermo-ageing'. This suggests the production of a *common* change so as to vary μ in the same sense in all the cases. A diminution of the particle-size due to thermo-ageing would appear to be a simple and plausible explanation of this phenomenon on general grounds. The refractivity of a colloidal solution depends upon the total length of the optical path which a given beam of light traverses while passing through the system. This would depend upon the refractive index of the colloid material, that of the continuous medium, the size (presumably the shape), the electrical charge of the particles and their ionic atmosphere. Of this, no general theory is available in the literature. Working out of particular consequences in relation to observed facts and the assumptions implied in the derivation would appear to be both legitimate and suggestive of further work. An increased dispersion of the colloid, that is, a diminution of the particle-size, for example, would increase the proportion of the colloid matter in the optical path ; it would, therefore, bring μ nearer to that characteristic of the dispersed phase, that is, increase it, since the refractive index of any of the suspended materials is greater than that of the dispersion medium (μ_D for water = 1·33204 at 30°). The observed influence on μ of 'thermo-ageing' is in agreement with this deduction. It is to be anticipated that a main result of the diminution of the micellar size will be an increase in the corresponding charge and therefore, the stability of the colloid. In this connection it is interesting to point out some of the results of Davies (*loc. cit.*) on the electrolytic coagulation of gold sols, which had been subjected previously to 'thermo-ageing'. He observed that when the sol was 'thermo-aged' for moderate periods and then mixed with electrolytes, the coagulation velocity diminished with the duration of 'thermo-ageing' which shows that the stability of the sol increased during the process. The reverse effect was also observed when 'thermo-ageing' was prolonged. This is to be expected since the frequency and intensity of collisions increase with temperature, which favour micellar coalescence. It must, however, be pointed out that the above considerations regarding the dependence of μ on the only factor treated, *viz.*, the particle-size are not without limitations of applicability. It has been found for example in the data for μ during coagulations reported elsewhere in this Journal (*loc. cit.*) that *while in the majority of the coagulations studied, μ diminished during the change, sufficiently numerous cases have been observed* (*ibid.*) *showing just the reverse effect.* Furthermore, the diminution of the coagulation rate at any rate in some cases of the thermo-aged sols examined by Davies (*loc. cit.*) might not inconceivably be due to reduction in the number of micells in unit volume, which might be brought about by an increase in the average particle-size due to coalescence during 'thermo-ageing'. In the absence of a comprehensive general theory of the refractivity of a colloid in terms of the relevant factors mentioned already, which can correlate these results, accumulation of more experimental data for μ under diverse conditions of micellar behaviour is the principal need of the present phase of the developement of the subject.

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Experiments on Resolution of Co-ordinated Inorganic Compounds into Optical Isomers. Co-ordinated Cadmium Compounds with Recemic and Active Propylenediamine.

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In continuation of our work on the complex triethylenediamine salts of cadmium (Neogi and Mukherjee, *J. Indian Chem. Soc.*, 1934, **11**, 225) stable complex tripropylene diamine salts of cadmium have now been prepared with the three varieties of propylenediamine (*d*, *l* and *r*). Attempts to resolve the racemic compounds have so far been unsuccessful.

Regarding the complex compounds of cadmium with *d*- and *l*-propylenediamine, *l*-propylenediamine gave *l*-compounds and *d*-propylenediamine gave *d*-compounds, and the properties are similar to those of the racemic varieties. Tschugaeff and Sokoloff (*Ber.*, 1907, **40**, 3461; *Ber.*, 1909, **42**, 55), however, obtained Pt, Pd and Ni compounds with opposite rotations with the two varieties of active propylenediamine. They themselves offered no explanation excepting the possibility of compounds with ring structure. It is, however, just possible that something in the nature of Walden inversion might have taken place.

EXPERIMENTAL.

Cadmium Tripropylenediamine Chloride was obtained by adding propylenediamine (10 g.) in small quantities to a well-cooled solution of cadmium chloride (8 g.) in water (10 g.). The clear solution deposited crystals on keeping in a vacuum desiccator. It crystallised from alcohol as white crystals, which are very soluble in water. [Found : N, 20·6; Cd, 27·6. $(\mathrm{Cd\ pn_3})\mathrm{Cl_2}$ requires N, 20·71; Cd 27·74 per cent].

Cadmium Tripropylenediamine Bromide was precipitated from a concentrated solution of cadmium tripropylenediamine chloride, by adding a solution of potassium bromide. It crystallised from alcohol as white crystals. It is less soluble in water than the chloride. [Found : N, 16·85 ; Cd 22·53. $(\mathrm{Cd\ pn_3})\mathrm{Br_2}$ requires N, 16·98 ; Cd, 22·75 per cent].

Cadmium Tripropylenediamine Iodide was precipitated by adding a saturated solution of potassium iodide to a concentrated solution of cadmium tripropylenediamine chloride. It crystallised from alcohol as white crystals soluble in acetone. [Found : N, 14·10; Cd, 19·06. $(\mathrm{Cd\,pn_3})\,\mathrm{I_2}$ requires N, 14·27; Cd, 19·1 per cent].

Cadmium Tripropylenediamine Thiocyanate, prepared by the action of potassium thiocyanate on the chloride, crystallised from alcohol. [Found : N, 18·45 ; Cd, 24·79. $(\mathrm{Cd\,pn_3})\,(\mathrm{CNS})_2$ requires N, 18·64 ; Cd, 25·0 per cent].

Cadmium Tripropylenediamine Camphor Nitronate.—To a solution of cadmium tripropylenediamine chloride (5 g.) in water (10 c.c.) was added 5 g. of sodio *d*-camphor nitronate, dissolved in 20 c.c. of water and the mixture well shaken. The solution was then subjected to fractional crystallisation in vacuum. The first fraction was recrystallised from water as very light needles. [Found : N, 14·88; Cd, 14·5; $\mathrm{H_2O}$, 4·7. $(\mathrm{Cd\,pn_3})\,(\mathrm{C_{10}H_{14}O_3N})_2,\ 2\mathrm{H_2O}$ requires N, 14·7; Cd, 14·75; $\mathrm{H_2O}$, 4·72 per cent].

$[\alpha]^{30}_{\mathrm{D}}$ of this substance in a dcm. tube with 5% solution was found to be +195°. The second fraction gave $[\alpha]^{30}_{\mathrm{D}} = +189°$ and the third gave $[\alpha]^{30}_{\mathrm{D}} = +185°$.

To a saturated solution of 3 g. of this substance, moderately dilute hydrochloric acid was added drop by drop and shaken till all the nitrocamphor had precipitated out which was filtered. To the filtrate excess of acetone was added whereby a small quantity of perfectly white tripropylenediamine cadmium chloride was precipitated which was allowed to settle. The supernatant liquid was then decanted off and the precipitate washed several times with acetone to remove all traces of the acid and any free nitrocamphor. It was then dissolved and examined in a polarimeter. The solution was found to be inactive. To a concentrated solution of the nitronate, a saturated solution of potassium bromide was added whereby the complex bromide was precipitated. After washing it first with a saturated solution of potassium bromide and then with water it was examined in a polarimeter. The solution was found to be inactive. Saturated solutions of potassium iodide and thiocyanate also precipitated the complex iodide and the thiocyanate respectively from the nitronate but these were also found to be inactive in water and acetone solutions.

Cadmium Tripropylenediamine Camphor Sulphonate was obtained by adding a solution of the silver salt of *d*-camphor sulphonic acid to a solution of 5 g. of cadmium tripropylenediamine chloride. The solution was filtered and evaporated in vacuum and fractionally crystallised, and the crystallised fractions gave a constant nitrogen content. [Found: N, 10·26; Cd, 13·21; H_2O, 1·94. $(Cd\,pn_3)\,(C_{10}H_{15}O_4S)_2$, H_2O requires N, 10·09; Cd, 13·5; H_2O, 2·16 per cent].

The values of $[\alpha]^{30}_D$ in a dcm. tube for all these fractions were $+23{\cdot}5°$. On acidifying a concentrated solution of any of these fractions with dilute HCl and adding excess of acetone, tripropylenediamine cadmium chloride was precipitated which was found to be inactive.

Cadmium Tripropylenediamine Bromocamphor Sulphonate.—To a solution of cadmium tripropylenediamine chloride (5 g.), a solution of the silver salt of *d*-bromocamphor sulphonic acid was added gradually till addition of one drop more caused no further precipitate. The solution was filtered, and the filtrate evaporated in vacuum and fractionally crystallised. All these recrystallised fractions gave the same nitrogen content. [Found: N, 8·2; Cd, 10·52; H_2O, 8·6 $(Cd\,pn_3\,C_{10}H_{14}BrSO_4)_2$, $5H_2O$ requires N, 8·04; Cd, 10·77; H_2O, 8·8 per cent].

Each of these fractions showed $[\alpha]^{30}_D$ in a dcm. tube $= +66°$. On acidifying concentrated solutions of these fractions with dilute HCl and adding acetone in excess, the complex cadmium chloride was precipitated which was found to be inactive.

Cadmium Tripropylenediamine Tartrate.—A concentrated solution of cadmium tripropylenediamine chloride (5 g.) was triturated with 4·5 g. of silver tartrate. The residue of silver chloride was repeatedly extracted with hot water and the extract evaporated in vacuum and various fractions were thus obtained and all on recrystallisation gave a constant nitrogen content. [Found: N, 15·82; Cd, 20·7; H_2O, 10·31. $(Cd\,pn_3)\,C_4H_4O_6$, $3H_2O$ requires N, 15·66; Cd, 21·0; H_2O, 10·1 per cent.]. Each of these fractions showed $[\alpha]^{30}_D$ in a dcm. tube $= +27{\cdot}5°$. The tartrate was converted into the corresponding chloride by means of barium chloride but in each case the resulting solution was inactive.

The compounds with *d*- and *l*-propylenediamine have been prepared in the same way as the racemic compounds.

Cadmium l-*Tripropylenediamine Chloride* was obtained by combining *l*-propylenediamine prepared from *r*-propylenediamine (*cf.* Baumann, *Ber.*, 1895, **28**, 1179; Tschugaeff, *ibid.*, 1907, **40**, 3461; 1909,

42, 55) with cadmium chloride. Ten per cent. solution in water gave $[\alpha]_{D}^{30}=37^\circ5$ $[M]=-11^\circ5$. [Found : N, 20·95; Cd, 27·45. Calc. N, 20·71; Cd, 27·74 per cent].

Cadmium l-*tripropylenediamine Bromide* was prepared as in the case of the *r*-variety. Ten per cent. solution of the bromide gave $[\alpha]_{D}^{30}=25^\circ8$ and $[M]=127^\circ5$. (Found : N, 16·90 ; Cd. 22·60. Calc. N, 16·98; Cd, 22·75 per cent].

Cadmium l-*Tripropylenediamine Iodide* was prepared in the same way as the inactive varieties. Ten per cent. solution gave $[\alpha]_{D}^{30}=26^\circ$, $[M]=153^\circ$. [Found : N, 14·41 ; Cd, 18·7. Calc. N, 14·27 ; Cd, 19·1 per cent].

Cadmium l-*Tripropylenediamine Thiocyanate.*—10% solution gave $[\alpha]_{D}^{30}=23{\cdot}5$. $[M]=106^\circ$. (Found: N, 18·77; Cd, 24·78; Calc. N, 18·64; Cd, 25·0 per cent.).

Cadmium d-*Tripropylenediamine Chloride,* prepared from cadmium chloride and *d*-tripropylenediamine (prepared from the *r*-variety, *cf.*, Baumann, *loc. cit.* ; Tschugaeff, *loc. cit.*). 10% solution gave $[\alpha]_{D}^{30}=+26^\circ$, $[M]=105^\circ$. (Found : N, 20·58 ; Cd, 27·53. Calc. N, 20·71; Cd, 27·74 per cent).

Cadmium d-*Propylenediamine Bromide.*—10% solution gave $[\alpha]_{D}^{30}=+26{\cdot}5^\circ$; $[M]=+131^\circ$. (Found : N, 17·2; Cd, 22·5; Calc. N, 16·98 ; Cd, 22·75 per cent.).

Cadmium d-*Propylenediamine Iodide.*—10% solution of the iodide gave $[\alpha]_{D}^{30}=+25^\circ$; $[M]=+147^\circ$. (Found : N, 14·39 ; Cd, 18·82. Calc. N, 14·27; Cd, 19·1 per cent.).

Cadmium d-*Propylenediamine Thiocyanate.*—$[\alpha]_{D}^{30}=+24{\cdot}7^\circ$; $[M]=+111^\circ$. (Found : N, 18·85; Cd, 25·08. Calc. N, 18·64; Cd, 25·0 per cent).

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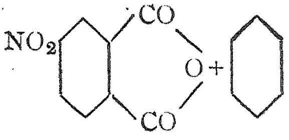
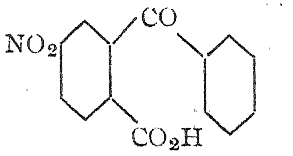
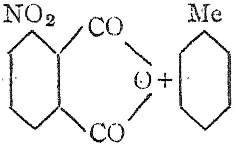
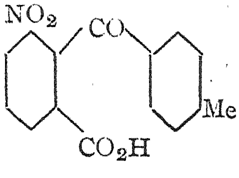
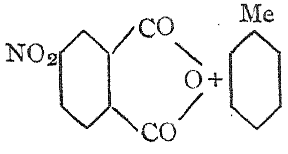
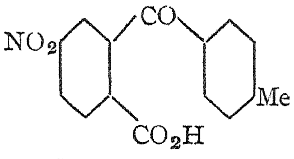
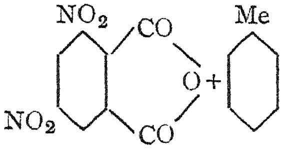
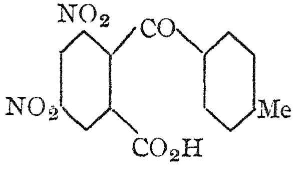
Condensation of 3- and 4-Nitrophthalic Anhydrides with Phenol and Anisole.

BY P. C. MITTER AND PHANINDRA NATH DUTT.

Of the various methods available for the synthesis of hydroxyanthraquinones, the condensation of nitrophthalic anhydrides with phenols and phenol ethers and the subsequent conversion of the resulting nitrobenzoylbenzoic acids into amino- and hydroxybenzoylbenzoic acids followed by ring-closing, is one of the most fruitful.

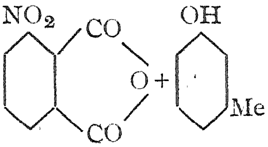
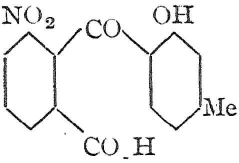
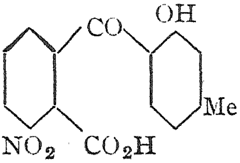
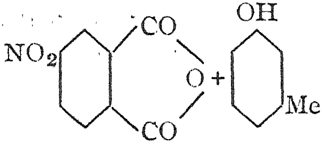
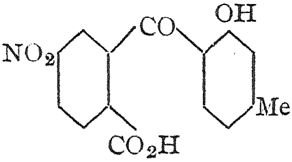
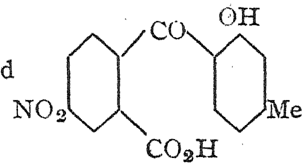
When phthalic anhydride condenses with phenols, the condensation takes place in such a way that the hydroxyl groups preferably take up the *ortho*-position with respect to the CO-group, though the *para*-linking also takes place to a limited extent. With phenolic ethers, however, linking is invariably in the *para*-position with respect to the alkyloxy group. In the case of nitrophthalic anhydrides a further complication is introduced by the presence of the nitro group, which exerts its own orienting influence. The present study was undertaken to ascertain the effect of such influence.

The following table gives the results of the condensation of 3- and 4-nitrophthalic anhydrides with benzene and toluene as determined by previous workers.

Components reacting.	Products obtained.	Authors and reference.,
		Rainer, *Monatsch.*, 1908, **29**, 178.
		Mitter and Sircar, *J. Indian Chem. Soc.*, 1930, **7**, 619.
		*ibid.*
		Mitter and Goswami, *J. Indian Chem. Soc.*, 1931, **8**, 686.

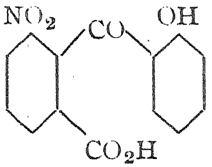
It would appear from the above that in the case of condensations with hydrocarbons, the CO-group nearer to the nitro group is more reactive than the other. The second component exerts little influence. Its influence becomes more marked, however, when the hydrocarbons are replaced by molecules having reactive groupings.

The following results have been obtained by previous workers in the condensations of 3- and 4-nitrophthalic anhydrides with phenols.

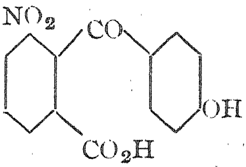
Components reacting.	Products obtained.	Authors and reference.
		Eder and Widmer, *Helv. Chim. Acta*, 1922, **5**, 3.
	and 	
		Mitter and Chatterjee, *J. Indian Chem. Soc.*, 1931, **8**, 784.
	and 	

It may be observed that in the case of condensation with 3-nitrophthalic anhydride, the quantity of the second isomer is very small in comparison with that of the first one.

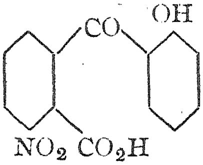
3-Nitrophthalic anhydride condenses with phenol in presence of aluminium chloride at 110-20° under the conditions employed by Eder and Widmer (*loc. cit.*) to give only one product, which may be one of the following four :—



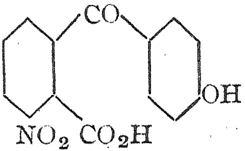
(I)



(II)



(III)

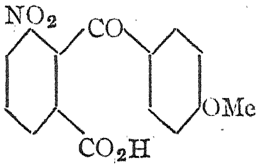


(IV)

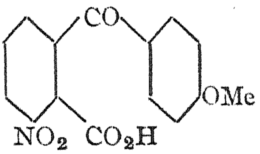
To determine the actual constitution, the nitro-acid is reduced to the corresponding amino-acid and then converted to the corresponding dihydroxy-acid by diazotisation. On heating with concentrated sulphuric acid and boric acid at the temperature of boiling water, the latter gave a dihydroxyanthraquinone identical with chrysazine. The constitution of the nitro-acid must therefore be (I).

Curiously enough, 4-nitrophthalic anhydride could not be condensed with phenol under any condition.

3-Nitrophthalic anhydride condenses readily with anisole with the formation of two products (V) and (VI), the former predominating.



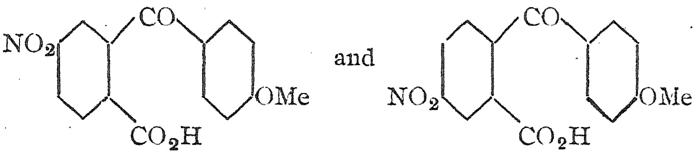
(V)



(VI)

The constitution of the first isomer was determined by converting it into 1:5-dihydroxyanthraquinone of Frobenius and Hepp (*Ber.*, 1907, **40**, 1048). The quantity of the other isomer being very small, its constitution could not be determined in the usual way by conversion into the corresponding dihydroxyanthraquinone. The constitution (VI) has been ascribed to it on the ground that while (V) easily gives the methyl ester by Victor Meyer's method, the second isomer was recovered unchanged even after refluxing for 2 hours with a methyl alcoholic solution of hydrochloric acid.

4-Nitrophthalic anhydride condenses with anisole at 20-25° in presence of aluminium chloride to give



Their constitutions have been determined in the usual way by conversions to 2:6- and 2:7-dihydroxyanthraquinones respectively.

EXPERIMENTAL.

3-Nitro-2-(2'-hydroxy)-benzoylbenzoic Acid.—3-Nitrophthalic anhydride (10 g.) was dissolved in redistilled phenol (100 c.c.) and heated to 110°-120° for ½ hour. Powdered aluminium chloride (20 g.) was gradually added and the mixture occasionally shaken. It was heated at 135° for 2½—3 hours when the mass almost solidified. It was decomposed with ice-water, hydrochloric acid (135 c.c., 10%) was added and heated on a water-bath; the excess of phenol was steam-distilled and the solid black mass was filtered and boiled with calcium carbonate repeatedly and the hot filtrate acidified with hydrochloric acid when the acid was precipitated. It was crystallised from dilute acetic acid as small yellow needles, m.p. 237-38°; yield 5-6 g. (Found: N, 4·97. $C_{14}H_9O_4N$ requires N, 4·87 per cent).

The *acetyl* derivative, prepared by heating with acetic anhydride and a drop of pyridine, crystallised from glacial acetic acid in shining colourless needles, m.p. 158°. (Found : N, 4·29. $C_{16}H_{11}O_7N$ requires N, 4·25 per cent.)

The *methyl ester*, obtained by passing dry hydrochloric acid gas into methyl alcoholic solution of benzoylbenzoic acid (1·5 g.) and refluxing on a water-bath for an hour, crystallised from ethyl acetate, m.p. 162°. (Found : N, 4·85. $C_{15}H_{11}O_6N$ requires N, 4·65 per cent).

3-Amino-2 (2'-hydroxy)-benzoylbenzoic Acid.—A warm solution of the nitrobenzoylbenzoic acid (4·5 g.) in concentrated ammonia (45 c.c.) was added to freshly precipitated ferrous hydroxide obtained from ferrous sulphate (32 g. in 210 c.c. of water and 50 c.c. of ammonia) and the mixture heated for 15 minutes and filtered. The filtrate was boiled to drive off ammonia and the solution boiled with a hot solution of alum (4·5 g. in 45 c.c. of water) and filtered, when prismatic yellow crystals (2 g.) were obtained. It was recrystallised from water, m.p. 217° (decomp.). (Found : N, 5·36. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent).

3-*Hydroxy-2-(2′-hydroxy)-benzoylbenzoic Acid*.— The amino-acid (2 g.) was dissolved in dilute ammonia by warming and dilute hydrochloric acid added until the precipitate first formed dissolved and on cooling, the hydrochloride was obtained in fine suspension. It was cooled and diazotised with a solution of sodium nitrite (0·7 g.). The precipitated diazo-salt was decomposed by boiling for 10-15 minutes, a little animal charcoal added and the solution filtered hot, when silky yellow needles (1·5 g.) were obtained. It was recrystallised from dilute alcohol, m.p. 199°-200°. It gives light pink colour with ferric chloride. (Found : C, 64·77 ; H, 4·12. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·86 per cent).

The *diacetyl* derivative, prepared by heating with acetic anhydride and a drop of pyridine for 3 hours, was crystallised from alcohol in colourless silky crystals, m.p. 186°. (Found: C, 62·98; H, 4·25. $C_{18}H_{14}O_7$ requires C, 63·1; H, 4·09 per cent).

1:8-*Dihydroxyanthraquinone* (*chrysazin*).—The dihydroxy-acid (2g.) was mixed with boric anhydride (2 g.), sulphuric acid (4 g., *d*, 1·84) and fuming sulphuric acid (20 g., 20% SO_3) and the mixture heated on a water-bath for 3 hours. This was then poured into ice and the orange mass was extracted with boiling water to remove boric acid and then with a cold 5% solution of sodium carbonate and finally crystallised from glacial acetic acid as bright golden yellow needles, m.p. 190-91° (*lit.* m.p. 191°). (Found: C, 70·45; H, 3·46. Calc. for $C_{14}H_8O_4$: C, 70·00; H, 3·33 per cent).

The *diacetyl* derivative crystallised from absolute alcohol as white needles, m.p. 230-32° (*lit.* m.p. 227-31°).

Condensation of Anisole with 3-Nitrophthalic Anhydride.

3-Nitrophthalic anhydride (10 g.) and anisole (100 c.c.) were treated in the cold under stirring with aluminium chloride (20 g.) and the mixture left overnight at the ordinary temperature. The deep red viscous mass was decomposed with ice-cold water and dilute hydrochloric acid and the excess of anisole distilled off with steam. The black tarry mass was extracted with dilute alkali, precipitated with acid, washed and boiled with calcium carbonate. The filtrate was acidified, and the red precipitate was dried and refluxed with benzene to remove the tarry product when an insoluble portion was left as flaky crystals. It was recrystallised from methyl alcohol, m.p. 214-15° (yield 0·9 g. from 10 g. of the mixture). The mother liquor was diluted with water and the precipitate crystallised from glacial acetic acid, m.p. 207° (yield 6-7 g. from 10 g. of the mixture).

3-*Nitro*-2-(4′-*methoxy*)-*benzoylbenzoic Acid*, (m. p. 207°) [Found: N, 4·25; OMe, 10·67. $C_{14}H_8O_5N(OMe)$ requires N, 4·6; OMe, 10·3 per cent].

The *methyl ester* melts at 123°. (Found: N, 4·69. $C_{16}H_{13}O_6N$ requires N, 4·44 per cent).

3-*Amino*-2-(4′-*methoxy*)-*benzoylbenzoic Acid.*—A warm solution of nitrobenzoylbenzoic acid (4·5 g.) in concentrated ammonia (45 c.c.) was added to the precipitated ferrous hydroxide from ferrous sulphate (32 g. in 210 c.c. of water and 50 c.c. of ammonia) and the mixture heated for 15 minutes and filtered. To the boiling solution a hot solution of alum was added and the solution filtered hot, when yellow crystals separated. It was recrystallised from dilute alcohol, m.p. 169-70°, yield 2 g. (Found: N, 5·16. $C_{15}H_{13}O_4N$ requires N, 5·18 per cent).

3-*Hydroxy*-2-(4′-*methoxy*)-*benzoylbenzoic Acid.*—The diazonium salt of the amino-acid was decomposed as usual and on filtration yellow needles with slight tarry matter were obtained. The crystals were washed with ether and recrystallised from dilute alcohol, m.p. 211-13°, yield 0·2 g. (Found: C, 66·5; H, 4·60. $C_{15}H_{12}O_5$ requires C, 66·7; H, 4·42 per cent).

1:6-*Dihydroxyanthraquinone.*—The crude anthraquinone was obtained by heating on a water-bath for 3 hours the above benzoylbenzoic acid (1 g.), boric anhydride (1 g.), sulphuric acid (*d* 1·84, 2 g. and 20% SO_3, 10 g) and removing the boric acid with boiling water and 5% sodium carbonate. It was intimately mixed with aluminium chloride (1 g.) and heated to 230° in the course of one hour and then kept at this temperature for half an hour more (*cf.* Mitter and Sircar, *J. Indian Chem. Soc.*, 1930, **7**, 628). The cold mixture was poured into acidified water and the residue dissolved in caustic potash and acidified. It crystallised from glacial acetic acid, m.p. 270-73°; diacetyl derivative, m.p. 230-4°.

6-*Nitro*-2-(4′-*methoxy*)-*benzoylbenzoic Acid*, m. p. 215°. (Found: N, 5·0; $C_{15}H_{11}O_6N$ requires N, 4·7 per cent).

6-*Amino*-2-(4′-*methoxy*)-*benzoylbenzoic Acid*, prepared from the nitro compound by reduction with ferrous sulphate and ammonia in the usual way, crystallised from absolute alcohol in needles, m.p. 186°. It gives bright red azo-compound when coupled with β-naphthol. It dissolves in alcohol with a yellow colour.

Condensation of Anisole with 4-Nitrophthalic Anhydride.

The anhydride (*cf.* Bogert and Boroschek, *J. Amer. Chem. Soc.*, 1901, **23**, 624; Mitter and Sircar, *loc. cit.*, p. 624) can be easily prepared by refluxing the nitro-acid with acetyl chloride for 1 hour. It does not require heating in vacuum at 190° until frothing ceases.

Aluminium chloride (40 g.) was gradually added to a well-stirred mixture of anhydride (20 g.) and redistilled anisole (200 c.c.) at 20-25°. The mixture was stirred for 2½ hours and then decomposed with powdered ice and dilute hydrochloric acid and the excess of anisole was distilled off with steam. The crystalline mass was repeatedly extracted with sodium carbonate and the filtrate acidified, when colourless shining needle-shaped crystals were obtained; yield, theoretical.

The crude acid (30 g.), after eight crystallisations from methyl alcohol, gave 2-(4'-*methoxy*)-*benzoyl*-4-*nitrobenzoic acid* of constant m.p. 217-18°. (Found: N, 4·73. $C_{15}H_{11}O_6N$ requires N, 4·66 per cent).

2-(4'-*Methoxy*)-*benzoyl*-5-*nitrobenzoic Acid* (2 g.) was obtained by diluting the methyl alcoholic mother liquor and repeated crystallisations (twelve times) from glacial acetic acid, m.p. 219-20°. (Found: N, 4·9. $C_{15}H_{11}O_6N$ requires N, 4·66 per cent).

Methyl-2-(4'-*methoxy*)-*benzoyl*-4-*nitrobenzoate* crystallised from ethyl acetate in shining plates, m.p. 178°. (Found: N, 4·7. $C_{16}H_{13}O_6N$ requires N, 4·5 per cent).

2-(4'-*Methoxy*)-*benzoyl*-4-*aminobenzoic Acid*, prepared by reducing the nitro-acid with ferrous hydroxide in the usual way, crystallised from water (charcoal) as yellow shining crystals, m.p. 156°, yield 0·2 g. (Found: N, 5·17. $C_{15}H_{13}O_4N$ requires N, 5·18 per cent).

2-(4'-*Methoxy*)-*benzoyl*-4-*hydroxybenzoic Acid*, prepared from the amino-acid as in the previous cases, was obtained as colourless needles from ethyl acetate and petroleum ether, m.p. 203°. (Found: C, 66·19; H, 4·6. $C_{15}H_{12}O_5$ requires C, 66·17; H, 4·42 per cent).

2:6-*Dihydroxyanthraquinone*.—The crude anthraquinone, obtained as usual from the above hydroxymethoxy-acid, was demethylated as in the case of 1:6-dihydroxyanthraquinone and the product crystallised from alcohol, m.p. above 365°. It sublimes at 200-250°/0·004, mm. in yellow needles. It gives a yellow colour with concentrated sulphuric acid and yellowish red colour with alkali.

The *diacetyl* derivative crystallised from glacial acetic acid, m.p. 221-25° (*lit.* m.p. 220-29°).

Methyl-2-(4′-methoxy)-benzoyl-5-nitrobenzoate crystallised from ethyl acetate as shining plates, m.p. 188°. (Found: N, 4·8. $C_{16}H_{13}O_6N$ requires N, 4·5 per cent).

2-(4′-*Methoxy*)-*benzoyl*-5-*aminobenzoic Acid* was obtained by reducing the corresponding nitro-acid with ferrous sulphate and ammonia. It crystallised ftom water (charcoal) as colourless needles, m.p.160°. (Found: N, 5·33. $C_{15}H_{13}O_4N$ requires N, 5·2 per cent).

2-(4′-*Methoxy*)-*benzoyl*-5-*hydroxybenzoic Acid* was obtained by diazotising a fine suspension of the hydrochloride in water and the precipitated diazo-salt was decomposed by boiling. It crystallised from ethyl acetate and petroleum ether as colourless microscopic crystals, m.p. 225°, yied 0·3 g. from 2 g. of amino-acid. (Found: C, 66·35; H, 4·7. $C_{15}H_{12}O_5$ requires C, 66·17; H, 4·41 per cent).

2:7-*Dihydroxyanthraquinone*, prepared as in the case of 1:6-dihydroxyanthraquinone, crystallised from alcohol as yellow needles, m.p. above 330° (diacetyl derivative, m.p. 189-91°). It dissolves in concentrated sulphuric acid with bluish red colour in the cold and a deep red colour when heated. It dissolves in alkali with deep red colour.

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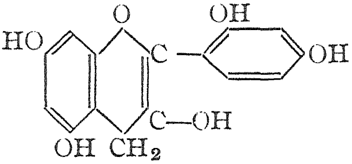
Studies in the *iso*Flavone Series.

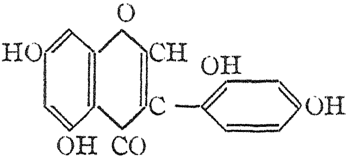
By P. C. Mitter and S. S. Maitra.

Consideration of the various evidences available as regards the chemical nature of cyanomaclurin led Perkin (*J. Chem. Soc.*, 1905, **87**, 721) to the formulation of a possible flavan structure for it, *viz.*,



Among the attempts which have been made to settle the constitution of cyanomaclurin, mention may be made of the researches of Bhalla and Ray (*J. Chem. Soc.*, 1933, 288); Appel and Robinson, (*ibid.*, 1935, 752), Mitter and Saha (*J. Indian Chem. Soc.*, 1934, **11**, 257) who considered the possibility of flavanone structure, but they could not establish this structure by a complete synthesis.

Within recent years a good number of *iso*flavones have been found to occur among plant products pertaining to both the tinctorial and non-tinctorial varieties, and it occurred to us that the possibility of an *iso*flavone structure for cyanomaclurin was worthy of consideration.



The formula ($C_{15}H_{10}O_6$) agrees fairly closely with the molecular formula of cyanomaclurin as determined by Perkin ($C_{15}H_{12}O_6$) and it also accounts for the fission products of the substance.

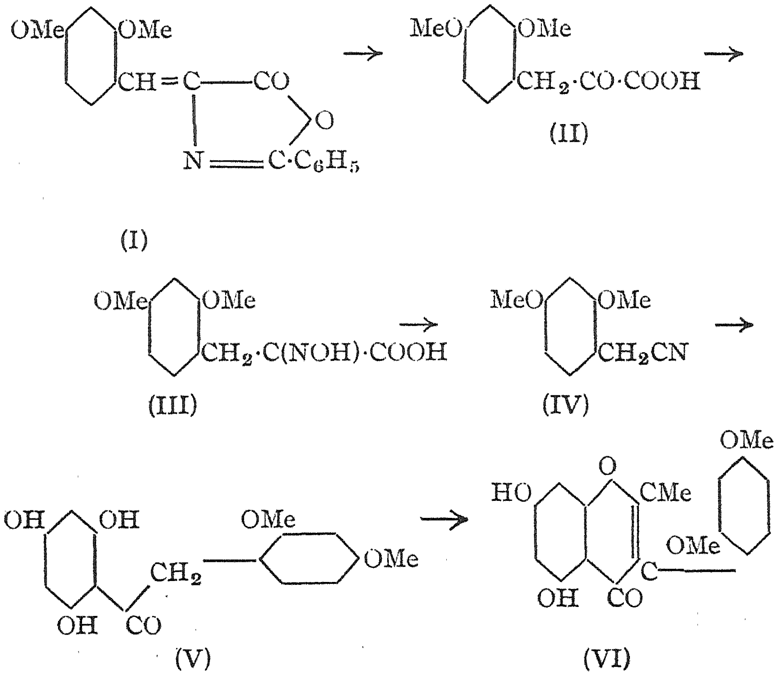
We, therefore, took up the synthesis of a substance of the above constitution, which even if it failed to give synthetic cyanomaclurin itself, would definitely exclude its *iso*flavone structure.

We started (*vide Proc. Indian Science Congress*, 1935, p. 153) from β-resorcyl aldehyde dimethylether which was obtained in good yield from resorcinol dimethylether according to the method of Adams and Montgomery (*J. Amer. Chem. Soc.*, 1924, **46**, 1518), later improved in our laboratory by Mitter and Saha (*loc. cit.*). We found, however, that the yield of the aldehyde could be still further improved by decomposing the imino-chloride first with ice and then with ice-cold hydrochloric acid in small quantities, for otherwise a considerable portion of the aldehyde is converted into tarry products. From the aldehyde the azlactone (I) was prepared which was hydrolysed into the corresponding pyruvic acid (II). This was converted into the nitrile (IV) over the oxime (III).

The nitrile was condensed with phloroglucinol by the method of Hoesch (*Ber.*, 1915, **48**, 1122) to give 2′:4′-dimethoxyphenyl-2 : 4 : 6-trimethoxyacetophenone (V).

Attempts of conversion of the substance into the corresponding *iso*flavone by the method of Späth and Lederer (*Ber.*, 1930, **63**, 743) as modified by Venkataraman and others (*J. Chem. Soc.*, 1934, 513, 1770) having failed, the corresponding 2-methyl*iso*flavone was prepared by the Allan-Robinson method (*J. Chem. Soc.*, 1924, **125**, 2192).

The *iso*flavone (VI) dissolved in concentrated sulphuric acid with a pinkish colouration. It gave with ferric chloride a transient violet colour which changes to dark brown after some time. On warming with dilute caustic soda solution no blue colouration was produced.


(I) (II) (III) (IV) (V) (VI)

EXPERIMENTAL.

Azlactone of β-Resorcylaldehyde Dimethylether (I).—It was prepared according to the method of Kropp and Decker (*Ber.*, 1909, **42**, 1186). β-Resorcylaldehyde dimethylether (16 g.), hippuric acid (17·5 g.) and fused sodium acetate (8 g.) were powdered to an intimate mixture and heated with 30 c.c. of acetic anhydride for 1 hour when the contents of the flask set to a fine deep yellow crystalline mass. A few c.c. of alcohol were added to the mixture while still warm and the contents triturated in a mortar. The thick paste was filtered at the pump and after washing successively with water, alcohol and benzol, recrystallised from alcohol or glacial acetic acid as yellow needles, m.p. 168° ; yield 17·5 g. (Found : N, 4·52. $C_{18}H_{15}O_4N$ requires N, 4·53 per cent).

2 : 4-*Dimethoxyphenylpyruvic Acid* (II).—The azlactone (10 g.) dissolved in 50 c.c. of 10% caustic soda solution was refluxed over a free flame for 4 hours. The solution, after cooling, was saturated with sulphur dioxide till the separation of benzoic acid was complete which was filtered after 24 hours. After crystallising twice from glacial acetic acid, it was obtained as colourless needles, m.p. 156°, which turned into a red sticky mass on exposure to air, yield 5 g. (Found : C, 59·05 ; H, 5·38. $C_{11}H_{12}O_5$ requires C, 58·92 ; H, 5·36 per cent).

The *oxime*.—The pyruvic acid (10 g.), hydroxylamine hydrochloride (8 g.) and 8% caustic soda solution (100 c.c.) were warmed to 50° for a few minutes and allowed to stand overnight. On acidification the oxime separated. It was crystallised from a mixture of ethyl acetate and petroleum ether, m. p. 145° (decomp.). (Found : N, 5·97. $C_{11}H_{13}O_5N$ requires N, 5·86 per cent).

2 : 4-*Dimethoxyphenylacetonitrile* (IV).—The dry oxime (10 g.) was heated with acetic anhydride (6 c.c.) on the water-bath and after the vigorous reaction had subsided (2-3 minutes), about 50 c.c. of water were added and the mixture shaken vigorously. The nitrile separated first as an oil, which soon solidified. On washing it with dilute sodium bicarbonate solution and crystallising it from rectified spirit, it was obtained as beautiful needles, m. p. 76°, yield 6 g. (Found : N, 8·01. $C_{10}H_{11}O_2N$ requires N, 7·9 per cent).

2′ : 4′-*Dimethoxyphenyl*-2 : 4 : 6-*trihydroxyacetophenone* (V).—Dry HCl gas was passed into an ice-cold ethereal solution of the dry nitrile (2 g.) and anhydrous phloroglucinol (2 g.) in 25 c.c. of ether containing freshly fused anhydrous zinc chloride (0·8 g.) until saturation. On keeping overnight, reddish orange crystals separated which were washed with ether and boiled about half an hour with 75 c.c. of water. On cooling the aqueous solution, colourless crystalline plates separated, which after recrystallisation melted at 175°. (Found : C, 63·24 ; H, 5·28. $C_{16}H_{16}O_6$ requires C, 63·15 ; H, 5·26 per cent).

The *dibenzyl* derivative, prepared by heating the ketone (3 g.), benzyl chloride (3 g.) and anhydrous potassium carbonate (3·6 g.) in dry acetone (45 c.c.) for 12 hours, separated as colourless needles from a mixture of alcohol and acetic acid, m.p. 135°, yield 0·8 g. (Found : C, 74·43 ; H, 5·9. $C_{30}H_{28}O_6$ requires C, 74·38 ; H, 5·8 per cent).

All attempts at condensation of the product with ethyl formate in presence of molecular sodium failed.

5 : 7-*Diacetoxy-2′ : 4′-dimethoxy-2-methyl*iso*flavone*.— The dry ketone (1 g.), fused sodium acetate (1 g.) and acetic anhydride (10 c.c.) were refluxed on an oil-bath at 175°-180° for 12 hours. The cold reaction product was treated with excess of dilute hydrochloric acid when oily drops separated, which solidified on keeping overnight. It was filtered, washed with dilute hydrochloric acid and crystallised from alcohol (charcoal) as colourless sandy crystals, m.p. 204°-205°. (Found: C, 63·97 ; H, 4·84. $C_{22}H_{20}O_8$ requires C, 64·07 ; H, 4·85 per cent).

5 : 7-*Dihydroxy-2′ : 4′-dimethoxy-2-methyl*iso*flavone* (VI).— The acetylated *iso*flavone (1 g.), dissolved in a few c.c. of 1% alcoholic potash, was warmed on the water-bath for 30-45 minutes. On acidification, a flocculent mass was obtained which crystallised from dilute alcohol (charcoal) as colourless sandy crystals, m. p. 213°-14°, yield 0·4 g. The *iso*flavone exhibited no fluorescence in aqueous alkali. (Found : C, 65·70 ; H, 4·76. $C_{18}H_{16}O_6$ requires C, 65·85 ; H, 4·87 per cent).

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Molecular Size of Cellulose from Different Sources. Part I.

By J. K. Chowdhury and T. P. Bardhan.

The problem of the identity of different celluloses was investigated in a *qualitative* manner by Chowdhury and Bose (*J. Indian Chem. Soc.*, 1932, **9**, 615) who concluded that they were all made up entirely of anhydroglucose units though the number of these units differed in different cases. One of the objects of the present investigations was to determine *quantitatively* the actual number of anhydroglucose units in different celluloses.

As is well known, Staudinger, from a careful study of viscosity measurements, found a relationship between viscosity and molecular weight of polymer homologues as expressed by

$$\eta_{sp}/C = k_m . M \qquad \ldots \qquad (i)$$

Where η_{sp} denotes specific viscosity, c, primary molar concentration, K_m, a constant for each polymer homologous series and M, the molecular weight. This formula has been verified in the case of hydrocarbons as well as synthetic polymers upto the molecular weight of about 10,000. It has been found that the molecular weights determined by this method as well as by the chemical and cryoscopic methods agree in a remarkable manner. By applying the K_m constant, determined from comparatively low molecular polymer homologues and checked by molecular weight determination by other methods, Staudinger obtained molecular weights as high as 200,000, a figure which cannot be even dreamt of by the application of other methods at our disposal

Though the formula is empirical in nature, Staudinger made an attempt to derive it, on certain assumptions, from the Einstein formula in the following manner :

$$\eta_c = \eta_o \left(1 + K_1 \frac{NQ}{V} \right) \qquad \ldots \qquad (ii)$$

where η_c denotes viscosity of the solution, η_o, the viscosity of solvent,

V, the total volume of solution, N, the number of solute molecules each of which has a volume Q, and K_1, a constant. Hence

$$\eta_c/\eta_o = \eta_r = 1 + K_1 \frac{NQ}{V}$$

or $$\eta_r - 1 = \eta_{sp} = K_1 \frac{NQ}{V}$$

where η_r is the relative viscosity and η_{sp}, the specific viscosity.

As $NM/V = C$ and $k = K_2M$, in the case of polymer homologues the equation may be given the following form :

$$\eta_{sp}/C = K_1 \frac{NQ}{V} \cdot \frac{V}{NM} = \frac{K_1 Q}{M} = \frac{K_1 . \pi r^2 h}{M}$$

$$= \frac{K_1 \pi r^2 K_2 M}{M} = K$$

where r denotes the radius and h, the length of the molecule.

Thus if Einstein formula were applicable to long fibre molecules, the specific viscosity should vary proportionately with concentration and would be independent of the number of molecules of the dispersed phase in polymer homologues so long as the diameter of the molecules remained the same, *i.e.*, the specific viscosity would not be affected if dissolved phase were divided into many small divisions or consisted of a few large molecules of the same diameter. This, however, is not found true by actual measurements of viscosity in the case of long fibre molecules which are found to have an altogether different relationship expressed by the empirical formula (*i*) of Staudinger.

Staudinger attempts to explain this inapplicability of Einstein formula in the case of fibre molecules by assuming that the total volume of the dissolved phase in the case of fibre molecules is not identical with the actual volume of these long molecules which, by their vibration, hinder the free motion of a part of the solvent and hence increase the viscosity abnormally. The total "effective volume" is, therefore, equal to the sum of the volume of the molecules and the volume of the immobilised solvent molecules.

This effective volume has been calculated by Staudinger by supposing the long fibre molecules to vibrate in such a manner that the total volume of its activity is equal to that of a flat cylinder having the diameter of the molecule as its height and the length as its diameter, so that the effective volume

$$Q_1 = \pi\left(\frac{h}{2}\right)^2 . \, 2r.$$

$$\text{Hence } \eta_{sp}/C = \frac{K_1 Q_1}{M} = \frac{K_1}{M} . \, \pi\left(\frac{h}{2}\right)^2 . \, 2r = \frac{K_1}{M} . \left(\frac{K_2 M}{2}\right)^2 . \pi . 2r$$

$$= \left(K_1 K_2^2 \, \pi \, \frac{2r}{4}\right) . \, M = K_m . \, M.$$

This assumption of the effective volume appears rather arbitrary. It cannot be understood why the effective volume should be like that of a flat cylinder instead of a sphere, as the large molecules are free to vibrate in all possible directions, specially in dilute solutions. The Staudinger formula must, therefore, be taken as entirely empirical and should not be applied without proper investigation.

EXPERIMENTAL.

Preparation of Standard Cellulose.—It is of essential importance that the different celluloses investigated should be as pure as possible and should be subjected to the same treatment if comparative results are aimed at.

The alcohol-benzol extracted cotton, delignified jute or bamboo was first extracted with a large volume of 1% caustic soda and then with boiling water (3 times). This was followed by alternate treatment with 17·5% caustic soda solution in the cold and 5% boiling caustic soda solution (5 times) with careful exclusion of air. The sample was then washed free from alkali and dried in air.

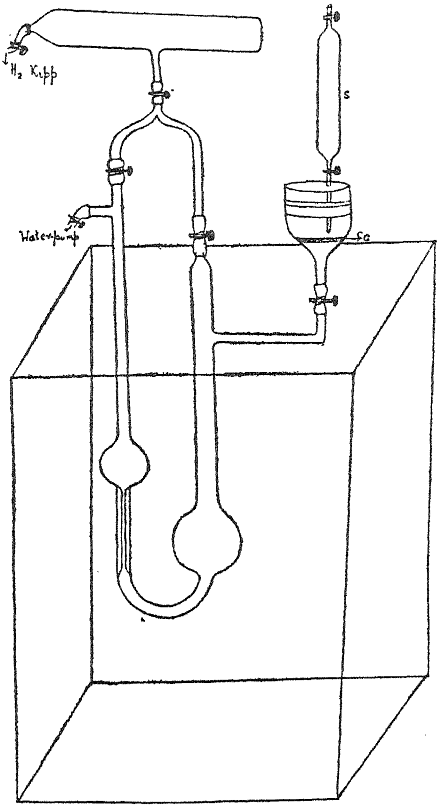
The analytical data of the different celluloses thus purified is given below.

TABLE I.

	Cotton.	Jute.	Bamboo.
Lignin	Nil	Nil	Nil
Furfural	1·17%	1·12%	1·2%
Fats and resins	Nil	Nil	Nil
Ash	0·05	0·23	0·52
Moisture	8·2	10·1	11·5
Uronic acid	Nil	Nil	Nil
Solubility in 17·5% alkali	1·95	1·92	2·2

Preparation of Schweitzer's Reagent.—The preparation of this solvent with a constant composition was effected by the method of Joyner (*Cellulose Chem.*, 1930, **11**, 105) slightly modified to suit new conditions. A glass jar (45 cm. × 10 cm.) was filled with clean copper turnings and then with liquor ammonia (29%) containing 1% cane sugar and was surrounded by a cold bath of ice. The jar was fitted with a reflux condenser and a mild stream of cooled air was continually passed through the solution for 24 to 26 hours. The solvent thus prepared was kept in a dark bottle in a cool place. The composition of the solvent was Cu = 30 ± 2 g./ litre and NH_3 = 165 ± 2 g./ litre.

FIG. 1.



G—Glass filter. S—Dissolving tube.

The arrangement described by the Cellulose Division of the American Chemical Society (*Ind. Eng. Chem.*, Anal. Ed., 1929, **1**, 50) was generally followed in order to effect the solution of cellulose in absence of air in Schweitzer's reagent. This solution was passed through a glass filter before leading it into the Ostwald tube.

Viscosity Measurements in an Inert Atmosphere.—The actual measurement of viscosity was carried out by means of an Ostwald tube (Fig. 1). A current of dry hydrogen was passed through the apparatus for about 30 minutes to ensure complete removal of air and by careful manipulation, a definite volume of the solution in the dissolving tube S was introduced into the Ostwald tube through the glass filter to remove traces of any mechanical impurity. The temperature of the thermostat was regulated up to ± 0·05°. The densities of the solutions were measured by means of a sp. gr. bottle.

Viscosity and Concentration.—It has already been mentioned that before applying the Staudinger formula for the determination of molecular weight, it is necessary to investigate the limit of concentration in which any relationship between viscosity and concentration can be established. According to the Einstein formula, viscosity should vary proportionately with concentration. It will be noticed from curve in Fig. 2 that this is true only in very dilute solution when the concentration is below 0·075% and viscosity below 1·9. As the concentration increases, the curve bends upwards showing that viscosity increases to a greater extent. This inapplicability of Einstein formula in the case of substances of high molecular weight has also been observed by other workers who attempted to put forward new formulæ showing relationship of viscosity and concentration but they were all empirical in nature and were applicable only within short ranges of concentration.

FIG. 2.

Cotton cellulose at 28°.

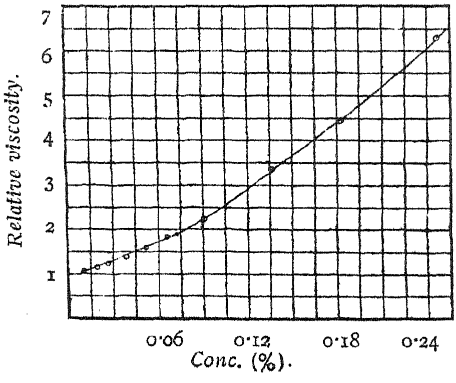
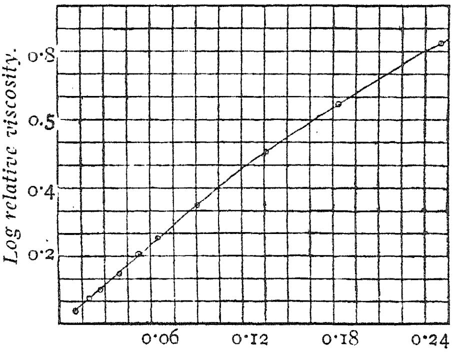


FIG. 3.

Cotton cellulose at 28°.



Conc. (%).

The steep rise of viscosity with higher concentration may be due to the action of one molecule on another, which increases the inner friction of the solution or to the volume of the solute being appreciable in comparison with the volume of the solvent. Following the same principles as those of Van der Waals in his modification of the gas laws, Mark and Fikentscher have tried to express this steep rise by the following modification of the Einstein fomula

$$\eta_r = 1 + \frac{K_1 NQ}{V - NQ}.$$

This modification, no doubt, explains the steep rise of viscosity with increase in the number of solute particles and hence with concentration. But this equation also fails to agree with actual facts if the concentration is varied within a wide range. Evidently it is only in very dilute solutions that any relationship between viscosity and concentration may be expected to hold. This is further reflected in the figures of molecular weights of cotton, jute, and bamboo celluloses which remain constant only when based on viscosity measurements at very low concentrations.

Molecular Weights of Different Celluloses.

The viscosity measurements were carried out at 28° and at 34° and the molecular weights were calculated with the help of the Staudinger formula, taking the value of K_m as 10×10^{-4}, the calculations being based on ash and moisture free cellulose.

It will be observed that the figures for molecular weights of cotton, jute and bamboo celluloses rise abruptly above the concentration of 0·042%, 0·058% and 0·122% respectively. As the change of temperature does not affect these figures, solvation or micelle formation does not seem to be the cause of such abnormal behaviour. The passing of the 'sol' solution to 'gel' solution as suggested by Staudinger or the influence of one molecule on the free vibration of another may possibly be responsible for such irregularity. It will be observed from Tables II-IV, that the molecular weight of cotton cellulose is 158200, that of jute cellulose 83680 and that of bamboo cellulose is 30590 approximately. The number of anhydroglucose units in these celluloses are, therefore, 978, 516 and 189 respectively.

FIG. 4.

Cellulose at 28°.

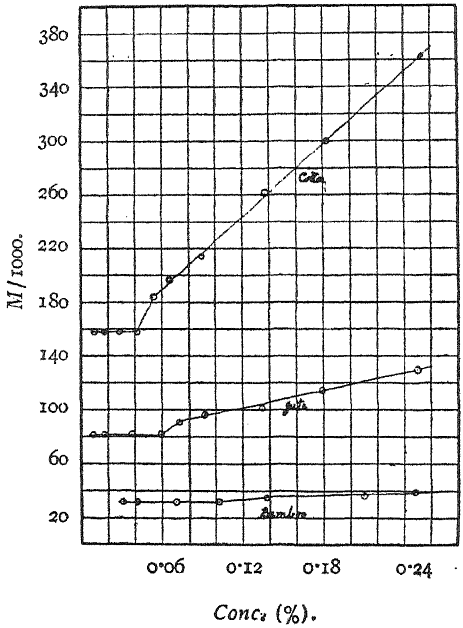


Fig. 5.

Viscose in NaOH *soln. at* 35°.

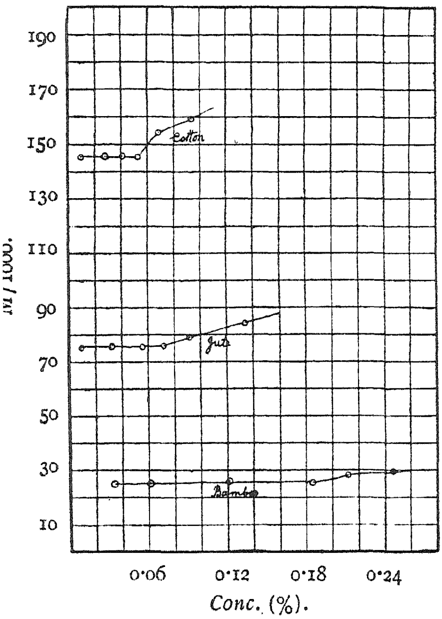


Fig. 6.

Cellulose triacetate in m-*cresole at* 24°.

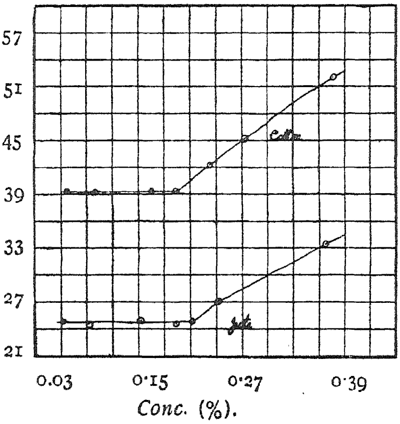


Table II.

Viscosity of cotton cellulose in Schweitzer's reagent.

Composition of the solvent = Cu, 28·5 g./litre ; NH_3, 161·2 g./litre.

Conc.	Primary mol. conc.	Temp = 28°.		Temp = 34°.	
		$\eta sp.$	M.W.	$\eta sp.$	M. W.
0·009175%	0·0005663	0·09	159000	0·09	159000
0·01835	0·001133	0·173	158000	0·178	157000
0·02752	0·001698	0·268	157800	0·267	157200
0·04129	0·002549	0·403	158100	0·403	158100
0·05321	0·003285	0·608	185100	0·611	186000
0·06422	0·003964	0·774	195300	0·770	194300
0·09175	0·005663	1·209	213700	1·209	213500
0·1376	0·008494	2·218	261100	2·211	260300
0·1835	0·01133	3·399	300000	3·465	385800
0·2569	0·0186	5·735	361600	5·722	360800

TABLE III.

Viscosity of jute cellulose in Schweitzer's reagent.

Composition of the solvent—same as in Table II.

		Temp = 28°.		Temp = 34°.	
Conc.	Primary mol. conc.	$\eta_{sp.}$	M. W.	$\eta_{sp.}$	M. W.
0·008967%	0·0005535	0·046	83120	0·045	84150
0·01794	0·001108	0·093	83950	0·093	83620
0·03588	0·002215	0·187	84410	0·188	84870
0·0583	0·003599	0·298	83260	0·302	83910
0·07176	0·004430	0·407	91870	0·410	92550
0·08967	0·005535	0·531	95940	0·529	96380
0·1346	0·008310	0·834	100300	0·834	100200
0·1794	0·01108	1·291	116500	1·284	115700
0·2512	0·01551	2·020	130200	2·016	130000

TABLE IV.

Viscosity of bamboo cellulose in Schweitzer's reagent.

Composition of the solvent = Cu, 30·2 g./litre; NH_3, 166 g./litre.

		Temp = 28°.		Temp = 35°.	
Conc.	Primary Mol. conc.	$\eta_{sp.}$	M. W.	$\eta_{sp.}$	M. W.
0·03250%	0·002173	0·067	31550	0·064	29450
0·06259	0·003802	0·1177	30770	0·117	30770
0·08798	0·005431	0·169	31120	0·165	30380
0·1215	0·007501	0·229	30520	0·2284	30450
0·1884	0·009779	0·328	33320	0·3287	33620
0·2112	0·01304	0·474	36360	0·4755	36500
0·2462	0·01520	0·600	39490	0·6034	39700

Molecular Weight of Cellulose in Viscose Solution.

In view of the industrial importance of viscose, the molecular weight of different celluloses in this solution was also investigated with the result that a somewhat lower value was obtained in this case though the same materials were used. Evidently, during the preparation of viscose, cellulose is to some extent disintegrated, the number of anhydroglucose units in cotton, jute and bamboo celluloses being 894, 468 and 158 respectively. Another interesting point is that the molecular weight remains constant to a somewhat higher range of concentration, *i.e.*, 0·054% , 0·072% , 0·185% respectively. This rise in limiting viscosity is in agreement with the partial degradation of the cellulose molecule.

A known weight of cellulose was dipped in CS_2 for 1 hour, the excess poured off and 20 c.c. of 16·91% NaOH solution were added and shaken for one hour. It was then made up to 100 c.c. with 4·94 % NaOH, 10 c. c. being added every half an hour. The solution was then diluted to 500 c. c. and filtered. Preparation of viscose and measurement of viscosity were completed in about the same time in all cases. Results are shown in Table V.

TABLE V.

Molecular weight of different celluloses in viscose.

Temp = 35°.

Material.	Conc.	Primary mol. conc.	$\eta_{sp.}$	M. W.
Cotton	0·009175%	0·0005663	0·082	144800
	0·02752	0·001698	0·247	145400
	0·04129	0·002549	0·37	145200
	0·05321	0·003285	0·473	144100
	0·06422	0·003924	0·603	153400
	0·09175	0·005663	0·899	158800
Jute	0·008967	0·0005535	0·042	75880
	0·03588	0·002215	0·169	76300
	0·0583	0·003599	0·270	75020
	0·07176	0·004430	0·339	76520
	0·08967	0·005335	0·439	79320
	0·1346	0·008310	0·693	83390
Bamboo	0·03520	0·002173	0·055	25310
	0·0615	0·003802	0·098	25770
	0·1215	0·007501	0·170	26150
	0·1848	0·01141	0·287	25160
	0·2112	0·01304	0·363	27840
	0·2462	0·01520	0·445	29280

Molecular Weight of Cellulose Triacetate in m-*Cresol*.

Determination of molecular weight in the case of cellulose acetate shows a further degradation during acetylation, though special care was taken to follow a method which would minimise degradation. As the acetate thus prepared was not completely soluble in ordinary solvents, *m*-cresol was used for the purpose and special care was taken to avoid absorption of water vapour by the solvent. The molecular weights of cotton acetate and jute acetate are found to be 39870, 24920 respectively, which give the number of anhydroglucose units in the case of cotton and jute as 138 and 86 respectively. In this case, the limiting concentration is still higher, being 0·16%, and 0·18% respectively in the case of cotton and jute acetates.

In acetylation, it was necessary to adopt a method which would not seriously affect the cellulose. For this purpose Barnett's method as modified in this laboratory (*J. Indian Chem. Soc.*, 1932, **9**, 618) was followed. The acetyl contents of the products were 43·85%, 43·2% in the case of cotton and jute respectively. The solution of the acetates were effected in distilled *m*-cresol. Measurements of viscosity was made after the solution had stood for sometime in the Ostwald tube.

TABLE VI.

Viscosity of cotton triacetate in m-*cresol.*

Conc.	Primary mol. conc.	Temp. = 28°.		Temp. = 34°.	
		η_{sp}.	M. W.	η_{sp}.	M. W.
0·035%	0·001215	0·053	39660	0·053	39660
0·067	0·002327	0·101	39460	0·103	40240
0·1082	0·003757	0·167	40410	0·166	40170
0·1604	0·005569	0·244	39950	0·245	39990
0·2008	0·006971	0·320	42900	0·330	43030
0·2412	0·008375	0·416	45150	0·418	45370
0·3476	0·01207	0·696	52420	0·700	52720

TABLE VII.

Viscosity of jute triacetate in m-*cresol.*

Conc.	Primary mol. conc.	Temp.=28°.		Temp =34°.	
		$\eta_{sp.}$	M. W.	$\eta_{sp.}$	M. W.
0·0315%	0·001099	0·0301	25100	0·0303	25200
0·0616	0·002139	0·058	24650	0·058	24650
0·123	0·004271	0·121	25870	0·120	25550
0·1638	0·005689	0·155	24770	0·152	24300
0·1812	0·006292	0·178	25710	0·174	25170
0·2134	0·007409	0·219	26870	0·220	27000
0·3421	0·01184	0·468	35920	0·467	33460

Molecular Weight of Degraded Cellulose.

If cellulose is treated with 42% HCl, at 0°, it is found that a white amorphous product, insoluble in water and in other ordinary solvents but soluble in Schweitzer's reagent, is obtained. The molecular weight of this product in Schweitzer's reagent (Table VIII) shows that cellulose molecules have been considerably disintegrated during the formation of this so-called cello-dextrin. The cello-dextrins from cotton and jute have molecular weights of 2088, and 1479 respectively and hence the number of anhydroglucose units are 13, and 9 respectively. This low number of anhydroglucose molecules explains the absence of fibre-structure in the degraded product.

10 G. of finely shreded cellulose were placed in a stoppered bottle and cooled in a refregerator for about 1 hour. About 350 c.c. of cooled 42% HCl were then added and the bottle kept in the refregerator for 7-8 hours with occasional shaking. At the end of this period all the cellulose had gone into solution which was then poured into about 2½ litres of cooled distilled water, when the product slowly separated and was allowed to stand overnight, washed free from acid and dried. As the product was very much degraded, comparatively stronger solutions were used for viscosity measurements.

TABLE VIII.

Viscosity of degradation product in Schweitzer's reagent.

Cu=28·8 g./litre; NH_3=165·4 g./litre. Temp.=35°.

Material.	Conc. cotton.	Primary mol. conc.	η_{spc}	M. W.
Cotton	1·9172%	0·09365	0·190	2124
	2·4213	0·1495	0·313	2093
	3·3065	0·2041	0·420	2058
Jute	1·3544	0·08373	0·1265	1510
	2·0186	0·1246	0·180	1445
	3·4215	0·2112	0·313	1482

CONCLUSION.

It is evident that the cellusoses from different sources are not identical and that their different physical properties are inherent in the size of the molecule and are not due to differences in physical conditions only. In Schweitzer's reagent, cotton, jute and bamboo are found to be composed of 978, 516 and 189 anhydroglucose units. In viscose, the cellulose is somewhat disintegrated, the cotton, jute and bamboo celluloses consisting of 894, 468 and 158 units of anhydroglucose. In acetylation, the disintegration proceeds further and the molecules are found to consist of 138, 86 residues of glucose in the cases of cotton and jute respectively. The disintegration can be carried still further by treatment with 42% HCl at 0°, when the molecules are found to consist of 13 and 9 glucose units only in the case of cotton and jute. The number of glucose units in native cotton cellulose is still higher and may be estimated as over 1000 anhydroglucose molecules, if the K_m constant, as experimentally determined by Staudinger in case of lower homologues, be applicable to the higher homologues as well.

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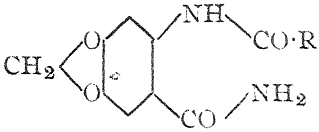
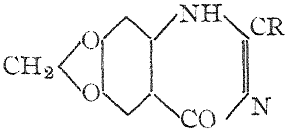
Quinazolines. Part IV.

By Sant Singh Bedi and Kartar Singh Narang.

Recently a number of alkaloids containing a quinazoline ring have been found in nature, *e.g.* vasicine, evodiamine, rutaecarpine, etc. In this paper some quinazolines are described prepared by the method indicated by Beri, Narang and Ray (*J. Indian Chem. Soc.*, 1935, **12**, 395). 6-Nitropiperonylamide has been reduced to 6-aminopiperonylamide (I). Condensation with suitable acid furnish the acyl derivatives (II) which easily cyclise to the quinazoline (III.)


(II)


(III).

EXPERIMENTAL.

6-*Nitropiperonal* was prepared by the method of Singh and Ray (*J. Indian Chem. Soc.*, 1930, **7**, 640).*

6-Nitropiperonal (5 g.) was oxidised in alkaline suspension with potassium permanganate solution (5%, 54 c.c.) during ½ hour with shaking at 40—60°. Finally the reaction was completed on the boiling water-bath for ¼ hour. The acid isolated in the usual way had m.p. 175° after crystallisation, yield 3·5 g.

6-*Nitropiperonyl Amide.*—6-Nitro-3:4-methylenedioxybenzoic acid (8 g.) suspended in thionyl chloride (20 c. c., freshly distilled) was refluxed on the steam-bath for ½ hour and then the excess of thionyl chloride removed in *vacuo.* The brownish yellow acid chloride was poured over ammonium carbonate (finely powdered, 25 g.) and the mixture heated on the steam-bath for ½ hour. After extraction with water, the nitroamide was obtained from the residue in brownish plates after crystallisation from hot water, m.p. 191-93°. [Found (after drying at 110°): N, 13·29. $C_8H_6O_5N_2$ requires N, 13·3 per cent).

6-*Aminopiperonyl Amide.*—The foregoing nitroamide (1 g.) was added in well powdered form to a solution of stannous chloride (3 g.) in hydrochloric acid (*d* 1·16, 3 c.c.) kept at 50—60°. The mixture was finally warmed to 70° for ½ hour and then cooled in ice. The separated tin double compound was dissolved in the smallest amount of water and basified in the ice cold and extracted with ethyl acetate. The residue after removal of the solvent crystallised from hot water, m. p. 172-74°. (Found: N, 15·43. $C_8H_8O_3N_2$ requires N, 15·5 per cent).

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* The nitration of veratric aldehyde described in this paper is incorrectly described to proceed at 5—10°. It should be at 30—35°. The yield is quantitative.

6-*Acetylamino-3:4-methylenedioxybenzamide.*—The foregoing amide (0·9 g.) and pyridine (0·4 g.) dissolved in benzene (5 c.c.) were treated with acetyl chloride (0·4 g.) and the mixture warmed for 10 minutes. After addition of water and removal of solvent, the product was crystallised from hot water, m. p. 212°. (Found: N, 12·5. $C_{10}H_{10}O_4N_2$ requires N, 12·6 per cent).

The *quinazoline* (III, R=Me) was prepared by dissolving the *acetylamino* compound (0·5 g.) in alcohol (25 c. c.) and treating the solution with sodium hydroxide solution (7·2 c. c., 1%). The mixture after warming to 40—50° for ½ hour was acidified with acetic acid and the product crystallised from water, m.p. 346°. (Found: N, 13·67. $C_{10}H_8O_3N_2$ requires N, 13·7 per cent).

The substance (II, R=$CH_2 \cdot CH_2 \cdot COOH$) was prepared by refluxing a mixture of 6-amino-3:4-methylenedioxybenzamide (0·9 g.), benzene (20 c.c.), and succinic anhydride (0·5 g.) for ½ hour. After cooling the *aminic* acid was filtered and then crystallised from water, m.p. 219°, yield 1 g. (Found: N, 10·16. $C_{12}H_{12}O_6N_2$ requires N, 10·0 per cent).

The substance (III, R=$CH_2 \cdot CH_2 \cdot COOH$) was prepared by dissolving the substance described above (0·8 g.) in sodium hydroxide (22 c.c., 1%) and warming the solution at 100° for ¼ hour. After acidification with acetic acid, the product was crystallised from hot water in silky needles, m. p. 271°, yield 0·65 g. (Found: N, 10·56. $C_{12}H_{10}O_5N_2$ requires N, 10·68 per cent).

Similarly, the butyryl derivatvies (II, R=$CH_2 \cdot CH_2 \cdot CH_3$) was prepared from butyryl chloride and the product crystallised in delicate needles from water, m.p. 184°. (Found: N, 11·3. $C_{12}H_{14}O_4N_2$ requires N, 11·6 per cent). It (0·7 g) was cyclised to III (R=*n*-propyl) in alcoholic solution (20 c c.) with 1% sodium hydroxide solution (1 mol.) on steam-bath by heating for ½ hour. The product, isolated as described before, crystallised from hot water in needles, m. p. 280°, yield 0·6 g. (Found: N, 12·1. Calc for $C_{12}H_{12}O_3N_2$: N, 12·06 per cent).

Most of ths analyses recorded above were done by the micro-method.

In conclusion we thank Prof. J. N. Rây for his interest in the work.

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Investigation on the Effects of Humidity and High Temperature on the NH_2-content of Different Samples of Rice.

By N. M. Basu and S. R. Maitra.

As rice stored up in dark, dingy go-downs during the rainy season when air is saturated with moisture at high temperature, becomes unhealthy and is believed to be one of the potent factors in the production of epidemic dropsy and since it is known that some amines, especially histamine, cause capillary dilatation leading to dropsy, which is the most prominent symptom of this disease, we thought that some amines might be produced in rice under this condition. Now if amines be actually produced in rice under these conditions, there would necessarily be an increase in its NH_2-content, although an increase in NH_2-content may not prove the formation of these poisonous amines. We accordingly wanted to see whether there is an increase in the NH_2-content of different samples of rice under these conditions, for if there be no increase in the NH_2-content, we may conclude that amines are also not produced.

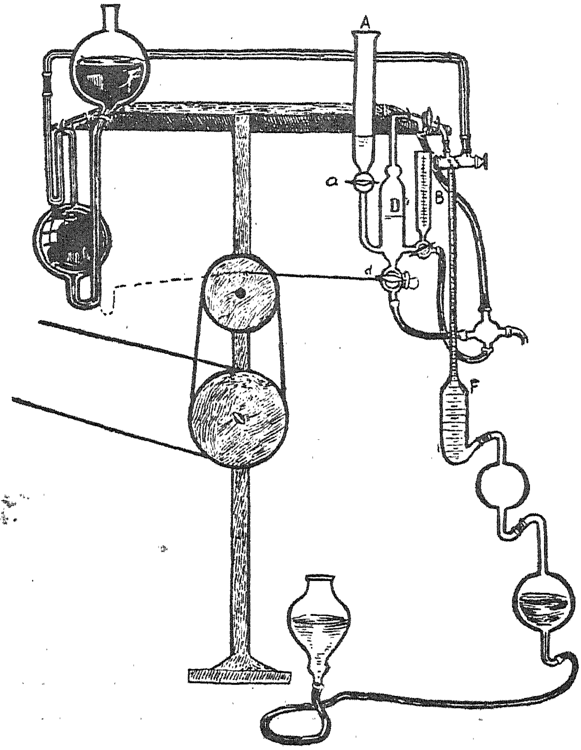
Various samples of rice freshly milled by indigenous method *(Dhenki-chata chal)* were obtained from Burdwan and fresh samples of milled rice from the College Street Market in Calcutta. They were kept in dry dishes in an incubator along with a dish of water so that the air inside was saturated with moisture and the temperature of the incubator was kept constant at 92° F. The samples of rice thus treated were examined, after every 4 or 5 days for a long period for their NH_2-N content by Van Slyke's method which has been slightly modified as given below.

EXPERIMENTAL.

As the method of making a dispersion of rice-powder for estimation of NH_2-N in Van Slyke's apparatus has been arrived at after a good deal of experimentation, it is worth while giving a resumè of the various preliminary attempts.

A suspension of rice-powder in normal saline was tried first but uniform results were not obtained owing to deposition of rice-powder in the reaction vessel and excessive frothing even in the presence of caprylic alcohol or liquid paraffin. The extract of the proteins of rice with 10% salt solution was next tried but the results were too low and the residue also contained protein. As rice contains considerable amount of glutaline (alkali soluble) and small amounts of alcohol-soluble prolamine, saline extract can never completely remove the proteins from rice. A dispersion of rice-powder in honey was subsequently tried but the results were not consistent as honey contains variable amounts of NH_2-N; gum-acacia was then used for making a dispersion of rice-powder, but the frothing was excessive and troublesome. The results were constant if the froth were taken to the Hempel pipette 2 or 3 times for absorption, caprylic alcohol were added once more after the first transference of the gas to the Hempel pipette and the shaking of the reaction vessel were done twice. Next the dispersion of rice-powder in dextrin solution was tried, and the results obtained were constant. There was practically no frothing so that caprylic alcohol need not be added more than once.

FIG. 1.



Procedure.

The gas burette F in Van Slyke's macro-apparatus is filled with water and the de-aminising bulb and the tube attached thereto are freed from air and filled with nitric oxide as is done in Van Slyke's method, the passage in the stop-cock connecting B and D being filled with $NaNO_2$ mixture. About 1 c. c. of caprylic alcohol is then carefully taken into D from B so as to avoid air bubbles. Now 2 grams of finely powdered rice are weighed accurately in a weighing bottle and transferred completely with a little 10% dextrin solution to an agate mortar in which the dispersion of rice-powder is made with the pestle by the addition of suitable amounts of dextrin solution. This dispersion is then transferred through a funnel to B of a micro-apparatus* and thence to D. The mortar, pestle and the funnel are now washed down with dextrin solution to B and then transferred to D, care being taken to prevent air bubbles from going inside D. The reaction vessel is now shaken for three minutes. The tap '*a*', is then turned on for a while so that the liquid rises in D upto a little below the bulb at the top of D for the transference of the major part of gas from D to F. The gas in F is then transferred to Hempel pipette. The connection between D and F is again restored. The reaction vessel is shaken once more for three minutes. The gas is now transfered to F with as much frothing as is possible by turning on *a*. The gas is once more removed to Hempel pipette which is then shaken for one minute. The remaining gas is next returned to F. As the gas that has collected in the meantime in D may contain a trace of nitrogen, it is once more transferred to F and thence to Hempel pipette which is again shaken for one minute. The remaining gas is then returned to F and the reading is taken. After about fifteen minutes the reading is once more taken and the volume obtained in the second reading is corrected to N. T. P.

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* We were using micro-apparatus at the beginning but owing to the following difficulties we selected the reaction vessel of the macro-apparatus and the gas burette of the micro-appratus to which 2 bulbs of 50 c c. each were attached :—

(*i*) The junctional tube between B and D in the micro-apparatus being very narrow, the thick colloidal dispersion of rice in dextrin solution cannot readily pass through to the de-aminising bulb. In the macro-apparatus this part is sufficiently wide.

(*ii*) De-aminising bulb in the macro-apparatus being much bigger, more space is obtained for the reaction to take place of a rather large volume of rice dispersion and accordingly the reaction is completed more readily.

(*iii*) The graduations in the burette of the macro-apparatus are not sufficiently fine and accordingly small differences in the volume of nitrogen which are generally noted in our estimations, cannot be detected. In the micro-apparatus these graduations are much finer and therefore answer our purpose very well. But the volumes of gases, *i.e.*, NO or N_2 accumulating in D and F become so large that these gases may escape by driving out the whole of water in the burette. To prevent this, two additional bulbs were attached in succession to the end of the burette F and connected by a rubber tube to the reservoir.

Results.—Four samples of milled rice and an equal number of *Dhenki*-hulled rice were examined for their NH_2-content at varying intervals after they were kept in the incubator. The results of these analysis are recorded in Table I and II. The figures in the tables refer to c.c. of nitrogen corrected to N. T. P. per 2 g. of rice.

TABLE I.

Milled rice.

Sample A.		Sample B.		Sample C.		Sample D.	
NH_2-N content.	No. of days.	NH_2-N content	No. of days.	NH_2-N content.	No. of days.	NH_2-N content.	No. of days.
2·48	Normal*	2·24	Normal*	2·18	Normal*	2·28	Normal
2·3	After 6 days	2·28	After 7 days	2·32	After 6 days	2·42	After 3 days
2·6	10	2·3	12	2·38	11	2·62	7
2·7	15	2·24	15	2·46	14	2·62	10
2·2	19	2·5	19	2·18	18	2·56	13
						2·5	18
						2·48	19

TABLE II.

Dhenki-hulled rice.

Sample I.		Sample II.		Sample III.		Sample IV.	
NH_2-N content.	No. of days.	NH_2-N content.	No. of days.	NH_2-N content.	No. of days.	NH_2-N content.	No.of days.
2·3	Normal*	2·12	Normal*	2·58	Normal*	2·6	Normal*
2·32	After 6 days	2·28	After 7 days	2·6	After 6 days	2·6	After 3 days
2·3	10	2·5	12	2·62	11	2·62	7
2·34	15	2·3	15	2·62	14	2·62	10
2·24	19	2·3	19	2·48	18	2·78	13
						2·72	18
						2·7	19

DISCUSSION.

From Tables I and II it appears that in samples B, C of milled rice and I, II, and III of Dhenki-hulled rice there is a gradual increase in NH_2-N, the longer the sample is kept in the thermostat, although this increase is much less marked in the case of Dhenki-hulled rice.

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* Before these were kept in the incubator.

It further appears that the amino-nitrogen having increased to a considerable extent, begins to fall abruptly.

In the case of sample A, there is a fall in the amount of nitrogen at the outset, then a rise which is followed by a diminution as in the case of other samples.

It is obvious that the rise in amino-nitrogen is due to the gradual decomposition of proteins of rice resulting in the formation of substances containing NH_2-radical. Whether these latter include amines or not, we cannot at present say definitely, for we have not as yet investigated that point. The subsequent fall in amino-nitrogen is probably due to the conversion of NH_2-radical into NH_3 and the liberation of the latter into air.

The peculiar behaviour of sample A may be due to the peculiar condition of this rice while it was under investigation. This rice appears to have been disintegrated and perforated, *i.e.*, the frame work has been already decomposed. Accordingly, substances containing NH_2-group have been already formed. When, therefore, it was placed in the thermostat in a moist atmosphere, NH_2 radical was soon converted into NH_3 and disappeared, resulting in a fall in amino-nitrogen after a few days. New surfaces within the rice were then exposed to the humid atmosphere; there was, therefore, further decomposition, resulting in an increase in amino-nitrogen. There would naturally be again a fall in amino-nitrogen owing to aforementioned reasons.

CONCLUSIONS.

It may be concluded that rice is decomposed in the rainy season with the production of substances containing NH_2-radical. Whether amines are formed we cannot at present definitely say. Further, Dhenki-hulled rice shows greater resistance to the action of humid atmosphere and high temperature than milled rice. This conclusion is corroborated by the following two facts we noticed. First, milled rice, after being exposed to humid atmosphere at a high temperature, can be more easily powdered than Dhenki-hulled rice. Secondly, it is very curious that in all bottles containing milled rice, some organism have grown, whereas these are absent in bottles containing Dhenki-hulled rice.

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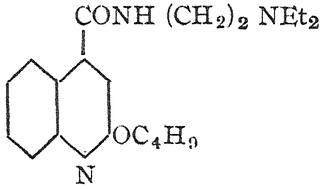
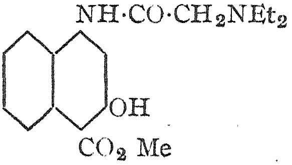
Quinoline Derivatives. Part IV.

By Kartar Singh Narang, Jnanendra Nath Ray and Thakur Das Sachdeva.

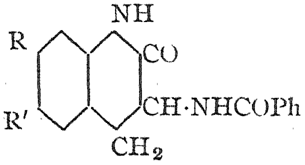
In nirvanine an acylamino group takes the place of usual benzoyloxy grouping of local anaesthetics. In percaine a similar grouping is noticeable and the ester grouping, so typical of this class of compounds, is missing. The basic part is a quinoline nucleus which can be the seat of local anaesthetic property (*cf.* Clemo and Perkin's tetrahydroquinolone, *J. Chem. Soc.*, 1924, **125**, 1608). Therefore it seemed of interest to prepare substance of the type (I).



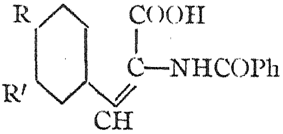
(Percaine)



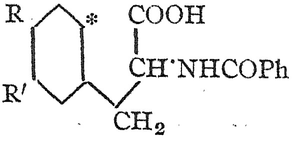
(Nirvanine)



(I)



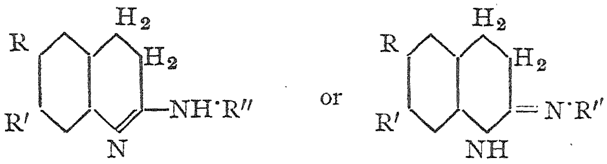
(II)



(III)

These have been prepared by the hydrolysis of the *azlactones* of varatric aldehyde and piperonal to the acids (II). These are easily reduced to the dihydro-acids (III), which as is usual with veratric aldehyde and piperonal derivatives nitrate in the 6-position (marked*) to give the corresponding 6-nitro-acids. These, on reduction, pass by simultaneous ring-closure to the 3-acylaminotetrahydroquinolones (I).

Attempts to prepare amidines (IV) were not successful.



(IV)

In view of the fact that 3:4-dihydroxyphenylalanine has been isolated from velvet beans (Miller, *J. Biol. Chem.*, 1920, **44**, 481) and the probability of substances of this type being the precursor of *iso*quinoline alkaloids in plants, we have prepared 3:4-methylenedioxyphenylalanine by the hydrolysis of (III). Dihydroxyphenylalanine has been previously prepared by Stephen and Weizmann (*J. Chem. Soc.*, 1914, **105**, 1152) by an indirect route.

EXPERIMENTAL.

The azlactone (4 g.) from veratric aldehyde and hippuric acid, suspended in potassium hydroxide solution (35 c.c., 3%) was heated for 10 minutes till a complete solution resulted. The well cooled solution was just acidified with acetic acid and the precipitate was crystallised from dilute alcohol in silky needles, m.p. 208°, yield 3·8 g. (Found: N, 4·37. $C_{18}H_{17}O_5N$ requires N, 4·28 per cent). The substance (II, R = R′ = OMe) is soluble in alkali carbonate solutions and reacts acid.

The foregoing acid (10 g.) was reduced with sodium amalgam (200 g., 2½ %) in a stoppered bottle with shaking and cooling. The alkaline solution furnished on acidification (III, R = R′ = OMe). The crude product was dissolved in ether and extracted with sodium bicarbonate solution whence on reacidification the substance was percipitated and then crystallised from hot water, m. p. 158°. (Found: N, 4·34. $C_{18}H_{19}O_5N$ requires N, 4·34 per cent).

The above described acid (2 g.) in acetic acid (10 c.c.) containing 3 drops of sulphuric acid (*d* 1·84) was treated with nitric acid (*d* 1·52, 2 c.c.) diluted with acetic acid (2 c. c.) at 50°. The product after standing for 15 minutes was poured on ice and the percipitate crystallised from alcohol in yellow silky needles, m. p. 208°, yield 1·1 g. (Found : N, 7·29. $C_{18}H_{18}O_7N_2$ requires N, 7·48 per cent).

A solution of foregoing β-6-nitro-3 : 4-dimethoxy-α-benzoylaminophenylpropionic acid (1 g.) was reduced with hydrated ferrous sulphate (10 g.) in water (15 c.c.) at 100° with ammonia for 45 minutes, the loss of ammonia being made good by fresh addition. The clear filtrate was well cooled and acidified with acetic acid. The separated solids and the residue from ether extraction of the mother liquor were crystallised from hot dilute acetic acid, m. p. 225°, yield 0·2 g. The substance does not contain a diazotisable amino group. (Found : N, 8·63. $C_{18}H_{18}O_4N_2$ requires N, 8·59 per cent).

The azlactone from piperonal and hippuric acid (4 g.) was hydrolysed as described before with potassium hydroxide solution (35 c. c., 3%). After acidification with acetic acid, the separated solids were crystallised from hot acetic acid, m.p. 224°. (Found: N, 4·59. $C_{17}H_{13}O_5N$ requires N, 4·50 per cent). The above acid on reduction with sodium amalgam furnished a product (III, R, R′ = O_2: CH_2), m. p. 122° after crystallisation from alcohol.

On nitration of the acid (2 g.) in acetic acid solution as described before, the nitro-acid, m. p. 210°, was obtained in yellow silky needles (1·1 g.). (Found : N, 7·56. $C_{17}H_{14}O_7N_2$ requires N, 7·82 per cent).

The nitro-acid (1 g.) was reduced with hydrated ferrous sulphate (10 g.) as described before. The mother liquor after acidification was extracted with chloroform in this case and the product was crystallised from alcohol, m. p. 254°, yield 0·2 g. (Found : N, 8·74. $C_{17}H_{14}O_4N_2$ requires N, 9·03 per cent).

Hydrolysis of β-3:4-Methylenedioxy-α-benzoylaminophenylpropionic Acid to β-3 : 4-Methylenedioxyphenylalanine Hydrochloride.—The acid (III, R, R′=O_2 : CH_2) (1 g.) suspended in hydrochloric acid (*d* 1·16, 50 c.c.) was heated at 100° for 4 hours, a few c.c. of acetic acid being added to facilitate solution. Hydrochloric acid (50 c. c.) was further added during the hydrolysis. The well cooled solution was extracted with ether and the aqueous portion then concentrated in a desiccator. The crystalline deposit of the amino-acid hydrochloride was collected, washed with ether and recrystallised from dilute hydrochloric acid, m. p. 278-80°, yield 0·1 g. (Found : N, 5·07 ; Cl, 13·1. $C_{10}H_{12}O_4NCl$, H_2O requires N, 5·31; Cl, 13·7 per cent.). The substance gave off water of crystallisation but it could not be satifactorily estimated owing to slight decomposition on prolonged heating at 120°.

The Anilide of 6-Nitro-3 : 4-methylenedioxycinnamic Acid.—6-Nitro-3 : 4-methylenedioxycinnamic acid (1 g.) was converted into its chloride in benzene solution with thionyl chloride. The solid acid chloride (without purification) was reacted with aniline in benzene solution. The anilide crystallised in needles from alcohol, m. p. 205°. (Found : N, 9·02. $C_{16}H_{12}O_5N_2$ requires N, 8·97 per cent). On reduction this substance did not gave the amidine as expected but was hydrolysed to 3 : 4-methylenedioxyquinolone, m. p. 205°. The structure was confirmed by synthesising the quinolone from 6-nitro-3 : 4-methylenedioxycinnamic acid by reduction as follows:—

1 G. of the 6-nitro-3 : 4-methylenedioxycinnamic acid dissolved in ammonia was reduced with ferrous sulphate (20 g.) in water (50 c.c.) on the steam-bath. The filtered solution on acidification gave the 3 : 4-methylenedioxyquinolone, m. p. 205° after crystallisation from alcohol. It does not contain a diazotisable amino or a carboxy group· (Found : N, 7·52. $C_{10}H_7O_3$ N requires N, 7·40 per cent).

Similarly β-3 : 4-methylenedioxy-6 - nitrophenylpropionic acid (Ahluwalia, Kaul and Ray, *J. Indian Chem. Soc* , 1933, **10**, 200) was converted into the chloride, which was then condensed with anthranilic acid in pyridine solution to β-3 : 4-methylenedioxy-6-nitrophenylpropionylanthranilic acid, m. p. 208° after crystallisation from acetic acid. (Found : N, 8·07. $C_{17}H_{14}O_7N_2$ requires N, 7·81 per cent). This substance also on reduction with ferrous sulphate in ammoniacal solution was hydrolysed to 3 : 4-methylenedioxytetrahydroquinolone (m. p. 232°), prepared for confirmation by the reduction of β-3 :4-methylenedioxy-6-nitrophenylpropionic acid with ferrous sulphate, m. p. 232° (mixed m. p. 232° with above). (Found : N, 7·25 $C_{10}H_9O_3$ N requires N, 7·33 per cent). The substance had no acidic properties nor it had diazotisable amino group.

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Chemical Examination of *Cuscuta Reflexa*, Roxb. Part III. The Constituents of the Oil from the Seeds.

By Radha Raman Agarwal and Sikhibhushan Dutt.

In two previous parts of this series the stem of the plant *Cuscuta reflexa*, which is commonly known as *Amarbel*, has been put to a thorough chemical examination (Agarwal and Dutt, *J. Indian Chem. Soc.*, 1935, **12**, 384, 586). The seeds of *Cuscuta reflexa*, which are commonly known as *Khasus* in vernacular, are also reputed to possess anthelmintic properties. In the present communication they have been put to a thorough chemical examination. The oil obtained by the benzene extract of the seeds has been worked up in details. The isolation and constitution of a yellow colouring matter belonging to flavone group is described in a subsequent paper. The oil consists of linolenic acid (9·92%), linolic acid (17·26%), oleic acid (25·58%), stearic acid (27·2%), palmitic acid (11·5%) and unsaponifiable matter (1·8%).

EXPERIMENTAL.

5·3 Kg. of the authentic dried sample were obtained from Amritsar (Punjab) and were crushed in a powerful crushing machine. The crushed material was then repeatedly extracted with boiling benzene in a big extraction flask. The combined benzene extracts were then concentrated in order to remove the solvent when it was obtained as a greenish yellow mobile liquid. On keeping it for about a week some white crystalline matter began to separate, which was filtered on a filter pump. It was recrystallised from boiling ethyl alcohol when practically colourless flakes were obtained (2·65 g.) which were identified as cuscutalin (Agarwal and Dutt, *J. Indian Chem. Soc.*, 1935, **12**, 384).

The oil was freed from traces of the solvent and purified by heating with animal charcoal and Fullers' earth on a water-bath. On filtration the oil was obtained as a transparant light greenish yellow liquid.

Examination of the Oil.—The oil contained no nitrogen or sulphur. It burnt with a sooty flame. On examination it was found to be a semi-drying oil since it became viscous on exposure to aerial oxidation. Table I contains the usual physical and chemical constants of the oil.

TABLE I.

Oil.

Sp. gr.	0·9352 at 23°
Refrac. Index	1·4820 at 25°
Solidifying pt.	−10°
Acid value	3·25
Sap. value	189·5
Acetyl value	17·4
Unsapon. matter	1·5—1·8%
Hehners' value	93·0
Iodine value	96·9

TABLE II.

Fatty acids.

Consistency	Solid
Sp. gr.	0·9026 at 25°.
Refrac. index	1·4639 at 25°.
Neutral value	192·9
Mean M. W	290·9
Iodine value	111·3

90 G. of the oil were then saponified in the usual manner and the unsaponifiable matter extracted with ether. The fatty acids were then liberated and purified (yield 80 g.). Table II gives the physical and chemical constants of the liberated mixed fatty acids.

The mixture of the fatty acids was then separated into the saturated and unsaturated acids by the Twitchells' lead salt-alcohol method (*Ind. Eng. Chem.*, 1921, **13**, 806) and Table III gives the percentage, iodine value and the mean molecular weight of the saturated and unsaturated acids.

TABLE III.

Acids.	Percentage in mixed acids.	Iodine value.	Mean M. W.
Saturated	41·32	3·02	265·6
Unsaturated	58·68	150·52	280·9

Examination of Unsatrated Acids·—10 G. of the unsaturated acids were dissolved in excess of caustic potash and oxidised by 2% aqueous solution of potassium permanganate in small instalments at the ordinary temperature. After the oxidation was complete, a current of sulphur dioxide was passed through the mixture. A white substance in flakes remained undissolved, which was filtered and extracted with ether. The ethereal extracts after the removal of ether deposited a crystalline substance as white flakes, m. p. 136°, and was identified as dihydroxystearic acid. The ether-insoluble portion was next extracted with boiling water and the extracts on cooling deposited white crystals, m. p. 172°, which proved to be tetrahydroxystearic acid. Traces of hexahydroxystearic acid were also present (m. p. 201°) in the original filtrate. The formation of these substances establishes the presence of linolenic, linolic and oleic acids in the unsaturated acids.

The quantitative estimation was next done by the bromine addition products by the method adopted by Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 1198; *cf.* also Agarwal and Dutt, *Proc. Acad. Sci. U. P.*, 1935, **5**, 227). A known weight of the unsaturated acids was dissolved in 150 c.c. of dry ether and treated with excess of bromine at −10° to −5°. On standing at this temperature for 2 hours a white precipitate of the linolenic hexabromide (m.p. 181°) separated which was filtered, washed and weighed. The excess of bromine was removed from the filtrate by thiosulphate, and the ether evaporated away. The residue was taken up with about 200 c.c. of dry petroleum ether and kept overnight. Linolic tetrabromide separated as fine glistening star-shaped needles (m. p. 112°) which was filtered, washed and dried. On concentrating the mother liquor a further crop of the tetrabromide was obtained which was added to the first and weighed. Finally the petroleum ether filtrate was evaporated to dryness and the bromine content of the residue determined.

TABLE IV.

Percentage of the various components.

Acids.	In unsaturated acids.	In mixed acids.	In the original oil.
Linolenic	18·62%	10·92%	9·92%
Linolic	32·51	19·07	17·26
Oleic	48·42	28·41	25·58

Examination of the Saturated Acids.—The mixture of the saturated acids (16 g.) was converted into their methyl esters and fractionally distilled under reduced pressure. The saponification values of the different fractions were determined and the mean molecular weights calculated. The acids were liberated from different fractions and melting points determined. The following table contains the results of these experiments.

TABLE V.

B. P. at 0·5 mm. pressure.	Wt.	Sap. value.	Mean M.W.	Acids		M.p. of liberated acid.
				Palmitic.	Stearic.	
160-170° rose to 180°	2·12 g.	204·1	274·0	1·68 g.	0·34 g.	63—64°
180-182° rose to 190°	1·80	200·0	280·5	1·09	0·64	
190-192°	4·63	192·5	291·5	1·08	3·32	64—65°
192-195° rose to 200°	4·80	190·1	295·2	0·52	4 05	67—68°
Residue.	2·21	189·5	296·0	0·18	1·92	66—67°
				4·55 g.	10·27 g.	

TABLE VI.

Acids.	In saturated acid.	In mixed acids.	In the oil.
Palmitic	30·71%	12·69%	11·5%
Stearic	69·29	28·63	27·2

Examination of the Unsaponifiable Matter.—The unsaponifiable matter was freed from the solvent when yellowish white waxy flakes were obtained. It was dissolved in water and repeatedly extracted with ether. The ethereal extracts were dehydrated with fused calcium chloride and the ether evaporated. The residue was once crystallised from acetone when colourless flakes were obtained, m. p. 126-128°. On recrystallisation from alcohol a phytosterol was obtained in fine silky needles, m. p. 134-35°. The acetyl derivative was prepared in the usual manner, m. p. 124-25°. The optical rotation of the sterol in chloroform solution was $[\alpha]_D^{20} = -30{\cdot}9°$.

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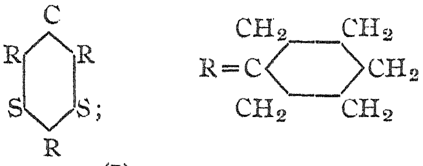
Studies on Cyclic Thioketones. Part I. Synthesis of Non-polymerised Thio*cyclo*hexanone, Thio*cyclo*pentanone and their Derivatives.

By Dines Chandra Sen.

The present paper describes the synthesis of thio*cyclo*hexanone, thio*cyclo*pentanone and their derivatives. These thioketones have been prepared by passing a simultaneous current of dry HCl and H_2S into an alcoholic solution of the corresponding ketones (*cf.* Sen, *J. Indian Chem. Soc.*, 1935, **12**, 647; *Science and Culture*, 1935, **1**, 158, 435). Fromm (*Ber.*, 1927, **60**, 2090) isolated tripolymerised thio derivatives by passing a successive current of HCl and H_2S into alcoholic solutions of *cyclo*hexanone, *cyclo*pentanone and *p*-methyl*cyclo*hexanone.



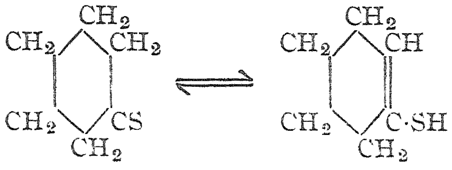
(I)

Trithio*cyclo*hexanone (I), as isolated by Fromm is a cyclic thioether and it does not react with phenylhydrazine, hydroxylamine, semicarbazide etc., nor can it be acylated or alkylated.

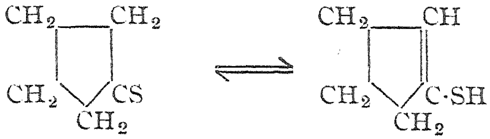
The function of hydrochloric acid in these cases seems to be three-fold; it acts (*i*) as a condensing agent, (*ii*) as a dehydrating agent and (*iii*) as a polymerising agent. Hence, Fromm could not isolate non-polymerised thioketones by passing successive currents of H_2S and HCl on account of accumulation of large excess of HCl. Non-polymerised thioketones could be isolated by taking out the thioketones as soon as they are formed from the zone of reaction, thus avoiding the influence of excess of HCl.

These thioketones when freshly distilled, are pink in colour, and the colour slowly changes to orange and finally disappears after a few days, but on redistillation, the pink colour reappears. If the pink colour be due to the chromophoric C : S group, then it follows that unlike cyclic ketones or ketonic esters, the thiolic phase of the cyclic thioketones is more stable at the ordinary temperature.

The 'thio-thiol' tautomerism in the above compounds, analogous to 'keto-enol' tautomerism in the corresponding ketones, has been observed and approximately estimated by iodometric method, Meyer's method of keto-enol estimation not being suitable.



(II) (III)



The iodometric method depends on the fact that the C·SH group will be oxidised whereas the C:S group will remain unchanged and that the addition of iodine to the double bond will be negligible compared to the oxidation of the thiol groups.

The formation of phenylhydrazones and semicarbazones identical with those of the corresponding ketones manifests the ketonic behaviour of the cyclic thioketones and it has been observed that the freshly distilled red liquids react more readily than the colourless thiolic varieties. Both thio*cyclo*hexanone and thio*cyclo*pentanone have been acetylated by the action of acetic anhydride in presence of sodium acetate giving *S*-acetyl derivatives since the products are coloured and since the acetyl groups are removed by phenylhydrazine in the cold producing acetyl phenylhydrazine and the phenyl hydrazones of the corresponding thioketones with evolution of H_2S.

The *cyclo*hexanone phenylhydrazone has also been converted to tetrahydrocarbazole by the action of dilute hydrochloric acid (*cf.* Bayer, *Annalen*, 1894, **278**, 106; Dreschel, *J. pr. Chem.*, 1888, *ii*, **38**, 67).

It has also been possible to prepare a colourless *S*-methyl derivative from the thio*cyclo*hexanone and it reacts with phenylhydrazine and gives methylmercaptan and *cyclo*hexanone phenylhydrazone.

It is noteworthy that the acetylated thioketones have got normal molecular weights in benzene (cryoscopic) whereas the parent compounds have molecular weights corresponding to nearly one and half times their normal values. This suggests that in benzene these free cyclic thioketones are most probably partly associated at low temperatures. However, it was not possible to determine the molecular weights by the boiling point method due to constant fluctuation of temperatures.

EXPERIMENTAL.

Thiocyclohexanone—A solution of *cyclo*hexanone (50 g.) in absolute alcohol (100 c.c.) was treated with a current of dry hydrochloric acid and dry sulphuretted hydrogen in the same manner as described in the case of thiocamphor (*cf.* Sen, *loc. cit.*). The solution slowly changed to deep red and suddenly after 1-1½ hours became turbid owing to the precipitation of an insoluble oil. The emulsion was treated with ice-cold water and extracted with ether, the ethereal solution was washed with water and sodium bicarbonate solution, dried over sodium sulphate, ether removed and the liquid distilled at 76°/15 mm., unchanged *cyclo*hexanone distiling at 45°/15 mm. Higher boiling fractions were also obtained whose investigations are not yet complete.

It is a heavy red oil having a slight mercaptanic smell, the colour slowly changing on keeping and ultimately becoming colourless. It slowly polymerises but the tripolymerised derivative is not easily formed without the agency of hydrochloric acid. It is insoluble in water and sparingly soluble in alcohol, but readily soluble in benzene, chloroform, ether, etc. It forms a yellow sodium salt with metallic sodium and a yellowish brown lead salt with lead acetate which immediately changes to black. [Found: C, 63·25; H, 8·65; S, 28·05; M.W. (in benzene, cryoscopic) 162. $C_6H_{10}S$ requires C, 63·16; H, 8·77; S, 28·07 per cent. M.W., 114).

The *semicarbazone*, prepared by the action of semicarbazide hydrochloride and sodium hydroxide, melts at 166°-67° (mixed m.p. with *cyclo*hexanone semicarbazone). (Found: N, 26·81. Calc. for $C_7H_{13}ON_3$: N, 27·09 per cent).

The *phenylhydrazone* was prepared by adding calculated amount of phenylhydrazine to the thioketone and keeping the mixture at the ordinary temperature overnight, when the liquid solidified and H_2S was evolved. Excess of phenylhydrazine was removed by washing with ether and the residue was crystallised from alcohol as plates, m.p. 75-76° (decomp.) (mixed m.p. with *cyclo*hexanone phenylhydrazone). (Found: N, 14·85. Calc. for $C_{12}H_{16}N_2$: N, 14·89 per cent). The phenylhydrazone with moderately concentrated hydrochloric acid forms *tetrahydrocarbazole*, which is obtained from *cyclo*hexanone phenylhydrazone. It crystallises from alcohol as needles, m.p. 120°. (Found: C, 83·72; H, 7·8; N, 8·15. Calc. for $C_{12}H_{13}N$: C, 84·21; H, 7·6; N, 8·19 per cent).

If the current of the two gases be continued for 3 hours, the whole solution becomes solid, which after crystallisation melts at 102°. It has been identified to be the trithio derivative of From (*loc. cit.*). (Found: C, 63·4; H, 8·71; S, 28·2; M.W. 348. Calc. for $C_{18}H_{30}S_3$: C, 63·16; H, 8·77; S, 28·07 per cent. M.W. 342).

*Methylation of Thio*cyclo*hexanone* : *Methyl*cyclo*hexane monosulphide*.—An ethereal solution of thio*cyclo*hexanone (10 g.) containing a few drops of alcohol was treated with metallic sodium (2·2 g.) in thin slices. The mixture was treated with methyl iodide (10 g.) and heated at 60°-70° for 2 hours. The solution was cooled, diluted with water and extracted with ether. From the ethereal solution the methyl derivative was obtained as a colourless liquid, b.p. 55°/15 mm. having a characteristic smell, yield 6 g.

The substance decolourises bromine water and dilute permanganate solution in cold. It does not form any precipitate with lead acetate. With phenylhydrazine it forms methyl mercaptan and *cyclo*hexanone phenylhydrazone. (Found: C, 65·25; H, 9·5; S, 24·85. $C_7H_{12}S$ requires, C, 65·62; H, 9·38; S, 25·0 per cent).

*Acetylation of Thio*cyclo*hexanone*.—Thio*cyclo*hexanone (10 g.), was heated with acetic anhydride (25 c.c.) and fused sodium acetate (5 g.) for one hour. The oil, separating on pouring the solution into water and making alkaline with sodium carbonate, was extracted with ether, the ethereal solution, dried over sodium sulphate, ether removed and then distilled at 85°/10 mm. It has an ester like smell, slightly pungent and on treatment with phenylhydrazine forms acetylated phenylhydrazine and cyclohexanone phenylhydrazone with evolution of sulphuretted hydrogen. It decolourises dilute bromine water and dilute permanganate solution in cold. (Found: C, 61·15; H, 8·05; S, 20·32; M.W. 159· $C_8H_{12}OS$ requires C, 61·54; H, 7·7; S, 20·51 per cent. M.W., 156).

*Thio*cyclo*pentanone* was prepared in a similar manner as described in the case of thio*cyclo*hexanone. Its odour is strongly mercaptanic. The tendency of formation of tripolymerised derivative is much greater in this case than in the case of thio*cyclo*hexanone. The insoluble red oil separates out in the course of 1—1½ hour, and even if it be treated just after the formation of emulsion by means of ice-cold water, nearly 5% of the material is changed into the tripolymerised derivative. It boils at 86°—88°/10 mm. (Found: C, 59·73; H, 8·25; S; 32·12; M.W. 142. C_5H_8S requires C, 60·0; H, 8·0; S, 32·0 per cent.M.W., 100). The tripolymerised derivative crystallises from alcohol as white shiny plates, m.p. 99°. (Found: C, 59·55; H, 7·99; S, 32·03; M.W., 310. Calc. for $C_{15}H_{24}S_3$: C, 60·0; H, 8·0; S, 32·0 per cent M.W., 300).

The *oxime* melts at 56°—57° (mixed m.p. with *cyclo*pentanone oxime). (Found: N, 14·23. Calc. for C_5H_9ON: N, 14·14 per cent).

The *semicarbazone* was very slowly formed by heating thio*cyclo*pentanone with semicarbazide hydrochloride and sodium hydroxide for 3-4 hours on the water-bath. It crystallised from alcohol as needles, m.p, 212°-13° (mixed m.p. with *cyclo*pentanone semicarbazone, Wallach, *Annalen*, 1907, **353**, 308). (Found: N, 30·31; Calc. for $C_6H_{11}ON_3$: N, 29·8 per cent).

The *acelyl* derivative, obtained in the same manner as in the case of thio*cyclo*hexanone, is a pungent smelling liquid, b.p. 67°/8mm. With phenylhydrazine in cold it gives acetyl phenylhydrazine (m.p. 128°), with evolution of H_2S, and a liquid (not isolated). (Found: C, 58·98; H, 7·21; S, 22·35; M.W. 142. $C_7H_{10}OS$ requires, C, 59·15; H, 7·04; S, 22·53 per cent. M.W. 142).

*Estimation of the Amount of Thio*cyclo*hexanone in the thiolic phase.*—Thio*cyclo*hexanone (0·4-0·5 g.) was dissolved in alcohol (50 c.c.) and heated with 25 c.c. of *N*/10-alcoholic solution of iodine at 10° and allowed to stand, the solution being constantly shaken. The excess of iodine was then titrated against *N*/10-sodium thiosulphate. 1 C.c. iodine absorbed=0·0114 g. of thio*cyclo*hexanone in the thiolic phase. The results found are 38% thiol in the freshly distilled sample and 70% after 1 hour.

In conclusion, I desire to express my sincere thanks to Sir P.C. Rây for his kind encouragement and also for the facilities in his laboratory.

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Diamagnetic Susceptibilities of Tin in Di and Tetra Valency States.

BY S. S. BHATNAGAR, M. B. NEVGI AND R. L. SHARMA.

Tin occurs in three different forms. Grey tin is cubic in structure while white tin is tetragonal. Further, white tin when cooled passes into the grey variety and when heated above 161° changes into the γ-phase. Honda (*Ann. Physik*, 1910, **32**, 1027) in his classical researches on the thermomagnetic properties of elements, has shown that white tin is paramagnetic, while grey tin is diamagnetic. He has further shown that the susceptibility of white tin undergoes a decrease on melting. Honda's work was further continued by Owen (*ibid.*, 1912, **37**, 657) who also found that white tin is paramagnetic ($\chi = +0{\cdot}02 \times 10^{-6}$) and grey tin is diamagnetic ($\chi = -0{\cdot}255 \times 10^{-6}$). Recently Ramchandra Rao (*Proc. Indian Acad. Sciences*, 1934, **1**, 123) has found that on powdering white tin becomes diamagnetic. Whether the change obtained by Rao is due to a change in the particle size or the conversion of tin into another allotropic modification due to pressure and temperature during the process of powdering, is a controversial matter. It appears, however, probable that a thermomagnetic investigation of the tin salts may throw some light on this unique behaviour of tin. Also a very desirable investigation would be the accurate determination of susceptibilities of tin ions in various valency states.

This publication deals with the last two aspects of the magnetochemistry of the tin ion.

EXPERIMENTAL.

The ionic susceptibilities in the dissolved state have been determined by the aid of a modified form of Decker's balance (Bhatnagar, Nevgi and Tuli, *Indian J. Phys.*, 1934, **9**, 311). In order to determine the susceptibilities at different temperatures, the portion of the tube between the upper stop-cock and the glass window is double-jacketted with an inlet and outlet for the circulation of water at different temperatures. The specific susceptibility in the dissolved state has been calculated according to the equation

$$\chi_L = \frac{\phi_L \left[\dfrac{\chi_w - \chi_a}{\phi_w - \phi_a} \right] + \left[\dfrac{\chi_a \phi_w - \chi_w \phi_a}{\phi_w - \phi_a} \right]}{d}$$

where χ_L, χ_a and χ_w denote respectively the mass susceptibility of the solution, of air and water ; ϕ_L, ϕ_a and ϕ_w denote the angle of torsion due to the solution, air and water respectively and d denotes the density of the solution.

The susceptibility of the salt from that of the solution has been calculated with the help of the relation,

$$\chi_L = \chi_{\text{salt}} \times C_{\text{salt}} + \chi_{\text{solvent}} \times (1 - C_{\text{salt}})$$

where C_{salt} denotes the concentration of the salt in solution.

The specific susceptibility of the salts in the solid state has been determined by a suitably modified form of Gouy's balance (*cf.* Nevgi, *Current Science*, 1935, 4, 403). For higher temperature measurements, an electric oven made of mica pieces and nicrom wire was used. According to the theory of this instrument, the susceptibilities can be calculated from the following equation.

$$\chi_{d_2} = \frac{1}{m_{d_2}} \left\{ (\chi_{d_1} m_{d_1} - \chi_a m_{ad_1}) \frac{W_{d_2}}{W_{d_1}} + \chi_a m_{ad_2} \right\}$$

where χ_a, χ_{d_1} and χ_{d_2} denote respectively the mass susceptibility of the medium (air), of the diamagnetic substance d_1, and d_2; m_{d_1}, m_{d_2}, denote masses of d_1 and d_2, and m_{ad_1} and m_{ad_2} that of air displaced by d_1 and d_2.

Estimation of the Purity of the Substances.

All the substances, which were used in this investigation, were extra pure. However, qualitative and quantitative analyses were always undertaken to test their purity. Only those substances which proved to be quite pure after going through this exhaustive process of analysis were employed for the magnetic measurements. A few of them had to be prepared in the laboratory.

The balance was tested against standard substances before its use in this investigation and the results obtained are given below.

TABLE I.

Substance.	$-\chi \times 10^{-6}$ at 25°.	$-\chi \times 10^{-6}$ at 60°.
NaCl	0·494	0·496
Aniline	0·688	0·690
Nitrobenzene	0·505	0·509

TABLE II.

Tin salts in the solid form.

Substance.	$-\chi \times 10^{-6}$ at 25°.	$-\chi \times 10^{-6}$ at 80°	$-\chi \times 10^{-6}$ (from Tables).
Stannous chloride	0·363	0·372	0·37
Stannic bromide	0·356	0·365	0·354
Stannic iodide	0·328	0·337	...
Stannous oxalate	0·251	0·264	...

TABLE III.

Tin salts from solutions (tried on Decker's balance).

Substance.	$-\chi \times 10^{-6}$ at 25°.	$-\chi \times 10^{-6}$ at 60°.
Stannous chloride	0·381	0·360
Stannic chloride	0·429	0·41
Stannic iodide	0·341	0·323

The ionic values of the negative radicals which are taken from the different authors are given below.

TABLE IV.

Bromine.	Iodine.	Chlorine.
$-32·5 \times 10^{-6}$ (Reichender)	-45×10^{-6} (Pascal)	$-22·1 \times 10^{-6}$ (Kido)
$-31·4 \times 10^{-6}$ (Farquharson)	......	$-20·1 \times 10^{-6}$ (Pascal)
......	......	$-19·85 \times 10^{-6}$ (Bhatnagar)

TABLE V.

The ionic values of tin.

Substance.	Ion.	Sources of the negative radical values.	Ionic values $-\chi \times 10^{-6}$.
$SnBr_4$	Sn^{IV}	Reichender Farquharson	26·0 30·5
SnI_4	Sn^{IV}	Pascal	25·5
$SnCl_2$	Sn^{II}	Kido Pascal Bhatnagar	24·67 28·67 29·17
Stannous oxalate	Sn^{II}	Pascal	22·9

DISCUSSION.

From a perusal of the above described results, it is evident that many interesting points arise. The general expression of the ionic susceptibility is

$$\chi_{\text{ion}} = - \frac{Ne^2}{6MC^2} \sum_n \bar{r}^2 \quad \ldots \quad \ldots \quad (i)$$

Slater (*Phys. Rev.*, 1930, **36**, 58) gave the following value for the radical part of the wave function of a single electron,

$$\psi = r^{(n'-1)} e^{-\left\{\frac{(z-s)}{n'}\right\} r}$$

and calcalated the mean square radius of the inert gases by the equation

$$\bar{r}^2 = \frac{n'^2 (n' + \frac{1}{2}) (n' + 1)}{(Z - S)^2}$$

where n' is the effective principle quantum number and $(Z-S)$, the effective nuclear charge. The electrons are divided into the following groups: 1s; 2s, p; 3s, p; 3d; 4s, p; 4d; 4f; etc. The screening constants are 0·35 for electrons in the same group (except for 1s electrons, where 0·30 is used); 0·85 and 1·0 for s and p electrons where $n = n_0 - 1$ and $N < N_0 - 1$ respectively. For d and f electrons, the value 1·0 should be taken for all electrons in the lower groups. After finding out the different values of $\bar{r}^2$ for all the electrons in an ion, the value of $\sum_n \bar{r}^2$ is substituted in equation (*i*) and the ionic value is determined.

The value of Sn^{IV} ion which belongs to the complete ionic configuration, has been calculated by Pauling (*Proc. Roy. Soc.*, 1927, **A114**, 181), Slater (*loc. cit.*), and Angus (*Proc. Roy. Soc.*, 1932, **A136**, 569) but the value of Sn^{II} does not seem to have been calculated. The rules followed by Slater (*loc. cit.*) and Angus (*loc. cit.*), although strictly valid for the configurations of complete ions, have been frequently employed to explain the magnetic behaviour of the ions which have not got the complete configuration. Accordingly an attempt has been made to calculate the value of Sn^{II} ion also.

According to the scheme given above the ionic value of Sn^{II} comes out to be $-38·247 \times 10^{-6}$. Recently Angus calculated the ionic value by taking into consideration a small difference in the screening constants of s and p electrons of the same quantum number. According to his formula the ionic value of Sn^{II} should be $-38·165 \times 10^{-6}$. In the following tables, the experimental and theoretical ionic values of Sn^{II} and Sn^{IV} are given as calculated from the results obtained here along with those given in the International Critical Tables. While calculating these values, the question of taking the correct values of the negative radicals comes in, but there is so great a discord between the values given by different authors that it has been found desirable to calculate the ionic susceptibilities by subtracting the different values of the negative ions from their molecular susceptibilities and bring into prominence their great divergence.

TABLE VI.

The ionic susceptibility of Sn^{IV}.

Substance.	Source.	The values of negative ions and their sources .		Ionic value $\chi \times 10^{-6}$.
		EXPERIMENTAL.		
$SnBr_4$	The present authors	Br = −32·5	Reichender	−26·0
		−31·4	Farquharson	−30·5
		34·7	Kido	−17·3
SnI_4	The present authors	I = −45·0	Pascal	−25·5
		−49·25	Ikenmeyer	− 8·5
		53·2	Kido	+7·3
$SnO(OH)_2$	International	Critical Tables		−28·0
$Sn(OH)_4$	International	Critical Tables		−34·4
$SnO(OH)CH_3$	International	Critical Tables		−28·1

THEORETICAL.

Slater	...	−23·838
Angus	...	−23·755
Pauling	...	−28·0

TABLE VII.

The ionic susceptibility of Sn^{II} .

Substance.	Source.	Values of the negative ions and their sources.		Ionic susceptibility $\chi \times 10^{-6}$.
		EXPERIMENTAL.		
$SnCl_2$	Present authors	Cl = −22·1	Kido	−24·67
		−20·1	Pascal	−28·67
		−19·85	Bhatnagar	−29·17
Stannous oxalate	,,	$\begin{matrix}\mathrm{COO}\\ \vert\\ \mathrm{COO}\end{matrix} = -0{\cdot}29$	Pascal	−22·9
$SnSO_4$	Int. Crit. Tables	SO_4 = −31·4	Int. Crit. Tables	−28·75
		−39·0	Kido	−21·15

THEORETICAL.

Slaters's method	...	−38·247
Angus' method	...	−38·165

From a survey of these tables it appears that the values of Sn^{IV} lie between 25·5 and 30·5 derived from the experimental results obtained here as against the theoretical values of 23·838, 23·755 and 28·0. The mean value of 25·5 and 30·5 comes out to be 28. This closely corresponds with the Pauling's value of 28. The values obtained by Slater and Angus are slightly lower. This difference seems to be due to the different values assigned to the negative ions. The ionic susceptibilities for Sn^{II} lie between 22·9 and 29·17. This is quite different from the theoretical values 38·247 and 38·165. It has been clearly pointed out by Angus and Kido that a disappointing feature of diamagnetic measurements is the lack of agreement between the results obtained by different authors who have investigated the same substance. This would become more evident from an examination of Table VIII which shows the divergence in the values of χ for various negative ions commonly reported in literature, and in the International Critical Tables.

TABLE VIII.

Diamagnetic ionic values of some common negative ions.

Author.	F.	Cl.	Br.	I.	SO_4.
		THEORETICAL.			
Pauling	8·1	29·0	54·0	80·0	51·0
Slater	8·3	25·79	40·1	59·83	...
Angus	7·25	22·86	36·65	55·32	...
Stoner	17·3	40·4	32·0	...	...
		EXPERIMENTAL.			
Kido	12·2	22·1	34·7	53·2	39·0
Ikenmeyer	13·9	20·4	34·8	49·25	...
Pascal	5·95	20·1	30·5	45·0	...
Bhatnagar	...	19·85	...	...	...
Reichender	...	21·9	32·5	...	...
Weiss	...	23·9	33·9	49·5	...
Farquharson	...	...	31·4	...	...
Int. Crit. Tables	...	...	...	...	31·4

Influence of Temperature.

From a survey of Table II it is evident that the diamagnetism of the tin salts increases with temperature. It has been shown by Honda that white tin decreases in its paramagnetism and becomes diamagnetic on melting. He has explained this phenomenon on the assumption that the magnetic susceptibility can be given by an expression

$$\chi = \chi_d + \chi_p$$

where χ_p and χ_d refer to the paramagnetic and diamagnetic contributions towards the susceptibility χ. χ_p has got a tendency to decrease with the rise of temperature. Consequently χ will increase in its diamagnetism. Recently Van Vleck (*Phys. Rev.*, 1928, **31**, 587; 1932, **14**, 1015), by the system of quantum mechanics, has developed an expression for molecular magnetism which can be written as

$$\chi = P_x + P_y - D$$

where P_x is paramagnetic dependent on temperature, P_y is a weak paramagnetic independent of temperature and D is pure diamagnetic. In substance where P_x is important, χ can have a tendency to increase in its diamagnetism with temperature. It seems probable that the increment obtained here with temperature might be due to the paramagnetic constituents of tin.

Solutions.

The diamagnetic values, recorded in Table III, for $SnCl_2$, $SnCl_4$ and SnI_4 in the dissolved state are slightly higher than those in the solid state. At higher temperatures, the diamagnetism of these salts in the dissolved state decreases to a certain extent. These changes, that have been observed here, can be attributed to some complex formation. Evidence in favour of complex formations is given below separately for each salt.

$SnCl_2$ *in Hydrochloric acid Solution.*—Water and hydrochloric acid play an important part in the formation of complexes with $SnCl_2$ independently or combined. According to the magnetic observations of Hoccard (*Compt. rend.*, 1929, **188**, 1151), Farquharson (*Phil. Mag.*, 1931, **12**, 283) and Scott and Blair (*J. Phys. Chem.*, 1933, **35**, 475), hydrochloric acid solutions of various concentrations themselves do not follow the mixture law. Engel (*Bull. Soc. chim.*, 1888, *ii*, **50**, 96) has shown that $SnCl_2$ combines with hydrochloric acid solution forming $HSnCl_3, 3H_2O$. $SnCl_2$ is said to form hydrates with one, two or four molecules of water in which dihydrate is the compound best known. Secondly, $SnCl_2$ itself exists in different forms under different conditions and in different solvents. $SnCl_2$ exists in the form of Sn_2Cl_4 in the vapour state as its vapour density is distinctly higher than the theoretical value. According to A. Werner (*Z. anorg. Chem.*, 1897, **15**, 1) the molecular weight of $SnCl_2$ is 202·8 in pyridine and 176 in ethyl sulphide while the calculated value is 189. Schröder and Steiner (*J. pr. Chem.*, 1909, *ii*, **49**, 63) found that the molecular weight is half the normal value in dilute solution of $SnCl_2$ in boiling methyl acetate. The freezing method of $SnCl_2$ in urethane (Castoro, *Gazzetta*, 1898, **28**, 317) shows that the molecular weight of $SnCl_2$ is normal. These facts point out the existence of different forms of $SnCl_2$ under different conditions and in different solvents. Thirdly, solution has got the tendency of absorbing oxygen from the atmosphere. The changes that are obtained may, therefore, be due to the above stated complexes.

$SnCl_4$ *Solution in Water.*—Union of $SnCl_4$ with water is attended by the development of heat, contraction in volume and the formation of several hydrates of $SnCl_4$ with water, amongst which $SnCl_4, 3H_2O$; $SnCl_4, 4H_2O$ and $SnCl_4, 8H_2O$ are well known. $SnCl_4, 8H_2O$ is stable between 19° and 56°; $SnCl_4, 4H_2O$ between 56° and 63° and $SnCl_4, 3H_2O$ between 63° and 83°. Kahlenberg and Lincoln (*J. Phys. Chem.*, 1899, **3**, 12) have found that $SnCl_4$ undergoes molecular association in some organic solvents. The decrease that is obtained here can be very easily explained on the view of the breaking up of these associations at higher temperatures.

SnI_4 *Solution in Benzene.*—The suitable solvent found for SnI_4 is benzene. SnI_4 is hydrolysed in water, and the other solvents such as CS_2, ether and chloroform have very low boiling points. These solvents cannot, therefore, be used here. Personne (*Compt. rend.*, 1862, **54**, 216) has noted that SnI_4 shows complex formation in benzene also. The decrease obtained at higher temperatures can, therefore, be attributed to breaking up of these complexes.

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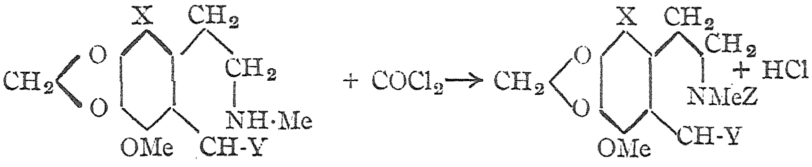
Studies in the Cotarnine Series. Part VI. Condensation of Cotarnine with Phosgene.

By B. B. Dey and (Miss) P. Lakshmi Kantam.

Cotarnine reacts readily with phosgene in the aldehydemine form and forms cotarnomethyl carbonyl chloride according to the following equation :



(I) (II)

(where $X = H$, $Y = O$, and $Z = CO{\cdot}Cl$)

The product is insoluble in acids and attempts to hydrolyse it to the carboxylic acid always led to decomposition into carbon dioxide, cotarnine being regenerated. The chlorine atom is rather unreactive and although hydrochloric acid was split off on boiling with water, it could not be made to condense with a second molecule of cotarnine to form dicotarnomethyl ketone or to take part in Friedel-Crafts' syntheses. It seemed to form an oxime under the usual conditions but on attempting to isolate it, the solution began to decompose with vigorous evolution of carbon dioxide. The methyl and the ethyl esters were, however, prepared with great ease and the presence of the free aldehyde group in these esters was shown by the formation of well characterised oximes and phenylhydrazones. The preparation of cotarnomethylurea by the action of ammonia on the chloride was not successful, but with aniline reaction occurred smoothly in the cold with the formation of the anil. It is interesting to note that in this reaction the chlorine did not react at all, but on warming with excess of aniline and keeping the mixture for 24 hours, carbanilide was obtained. A similar observation has been made in the case of cotarnomethylphenylurea (Dey and Kantam, *J. Indian Chem. Soc.*, 1934, **11**, 839). Neither in cotarnomethylcarbonyl chloride nor in the esters could the free aldehyde group be made to condense with compounds having a reactive methylene group, *e.g.*, nitromethane, phenylacetic acid, etc. Analogous derivatives have been prepared from 5-bromocotarnine and phosgene.

EXPERIMENTAL.

Cotarnomethylcarbonyl Chloride.—Cotarnine (2 g.) was suspended in 2*N*-NaOH (20 c. c.), a 20% solution of phosgene in toluene quickly added and the mixture vigorously shaken and cooled under the tap. The upper toluene layer which contained the product of reaction was separated after 2 hours and the toluene allowed to evaporate spontaneously. The solid obtained from the toluene was washed with dilute hydrochloric acid and dried on plate, the crude product weighing 2·5 g. Crystallisation from benzene and petroleum ether gave beautiful clusters of colourless flat prisms, m.p. 106°. (Found: C, 51·73; H, 4·80; N, 5·0; Cl, 11·62. $C_{13}H_{14}O_5NCl$ requires, C, 52·10; H, 4·70; N, 4·67; Cl, 11·84 per cent).

The product is insoluble in cold water but dissolves in hot water with decomposition, the solution precipitating silver chloride with silver nitrate. The chlorine is remarkably unreactive and on dissolving in hot alcohol and quickly cooling, the product crystallises out unchanged. On warming with baryta, a clear solution was obtained momentarily and then a precipitate of barium carbonate appeared. On acidifying and adding picric acid, cotarnine picrate crystallised out, m. p. and mixed m. p. 143°.

Ethyl Ester of Cotarnomethylcarboxylic Acid (II, X=H, Y=O, Z=COOEt).—The chloride was boiled for an hour under reflux with excess of alcohol, the alcohol mostly distilled off and the solution poured into water. The precipitated solid crystallised from 30% alcohol in clusters of colourless needles, m. p. 100°. (Found : C, 57·94; H, 5·79; N, 4·76. $C_{15}H_{19}O_6N$ requires C, 58·23; H, 6·14; N, 4·53 per cent).

The *Methyl ester*, prepared in the same way, crystallised in soft needles, m.p. 139°. (Found: N, 4·60. $C_{14}H_{17}O_6N$ requires N, 4·74 per cent).

The *Oxime* of the ethyl ester was prepared by suspending the latter (1 g.) in rectified spirit (5 c.c.), warming to 50° and quickly adding a solution of hydroxylamine hydrochloride (0·5 g.) and sodium acetate (1 g.) in water (5 c.c.). An almost clear solution resulted and on stirring for a few minutes, crystals of the oxime separated out.

Crystallisation from alcohol gave a product, m.p. 129°. (Found: N, 8·83. $C_{15}H_{20}O_6N_2$ requires N, 8·64 per cent).

The oxime dissolved in alkali and was reprecipitated unchanged on the addition of acids. It formed an *acetyl* derivative on rubbing with acetic anhydride, crystallising from dilute alcohol in short needles, m.p. 127°.

The *Phenylhydrazone*, prepared in the usual way, separated from alcohol in colourless glistening needles, m. p. 120°.

Anil of Cotarnomethyl carbonyl Chloride (II, X=H, Y=N·Ph and Z=CO·Cl).—The components were rubbed together in molecular proportions. Reaction occurred at once with evolution of heat and the anil separated out. The product was washed with dilute acetic acid and crystallised from acetone as colourless needles, m.p. 132°. (Found : N, 7·48; Cl, 10·10. $C_{19}H_{19}O_4N_2Cl$ requires N, 7·47; Cl, 9·46 per cent).

The anil is remarkably stable and it is not easily hydrolysed. When equivalent quantities of the anil and aniline were mixed together and left for a day and the clear solution treated with dilute acetic acid, considerable amounts of a white solid separated out which crystallised from alcohol in needles, m.p. 238°. It was shown to be carbanilide by m.p. and mixed m.p.

5-*Bromocotarnomethylcarbonyl Chloride* (II, X=Br, Y=O, Z=CO·Cl).—It was prepared from 5-bromocotarnine by the same method in excellent yield. It crystallised best from a mixture of chloroform and petroleum ether in hard colourless plates, m.p. 142°. (Found: N, 3·81. $C_{13}H_{13}O_5NBrCl$ requires N, 3·70 per cent).

The *Ethyl ester* crystallised in soft, colourless prismatic needles, m.p. 90°. (Found: N, 3·85. $C_{15}H_{18}O_6NBr$ requires N, 3·61 per cent).

The *Oxime*, m.p. 155°, was prepared in the usual way. It dissolved unchanged in cold alkali. (Found: N, 7·17. $C_{15}H_{19}O_6N_2Br$ requires N, 6·95 per cent).

The *Phenylhydrazone* crystallised from excess of boiling alcohol in colourless prismatic needles, m.p. 165°.

The *Anil*, m.p. 149°, was prepared as above. It also gave carbanilide on treatment with excess of aniline. (Found: N, 6·52. $C_{19}H_{18}O_4N_2BrCl$ requires N, 6·18 per cent).

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Influence of Dilution on the Molecular Refractivities of Complex Cyanides and Cobalt Amines.

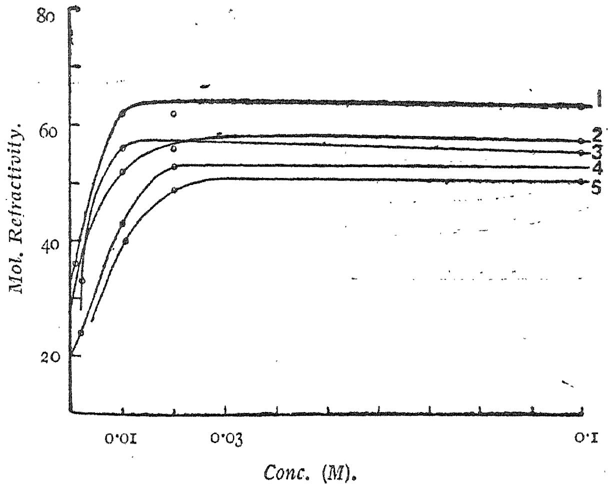
By Abani K. Bhattacharya.

It has long been known that the refractivity of inorganic salts in the solid state is approximately equal to that of their dilute solutions (Heydweiller, *Ann. Physik*, 1913, **41**, 520 ; *Physikal. Z.*, 1925, **26**, 526), and Fajans and Kohner, (*Z. physikal. Chem.*, 1930, **A**, **147**, 241) when the salts are split up completely into ions and their refractivities behave strictly in an additive manner. Prominent workers in course of their investigations have, however, made many anomalous observations where the values of the molecular refractivity were not strictly additive ; neither there was a regular order of variation in the molecular refractivities of many simple inorganic salts as the dilution was progressively altered. With a view to study the behaviour of the complex inorganic molecules with regard to their molecular refractivity at various dilutions (namely concentrations), a series of experiments was carried out by means of a Pulfrich refractometer and the results, calculated from the observations made under uniform conditions as far as possible, are being communicated through this paper for publication.

EXPERIMENTAL.

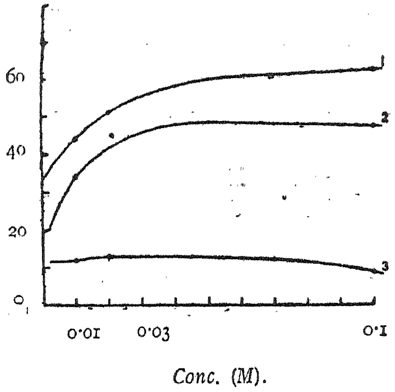
Pure salts of complex cyanides and cobalt ammines were taken and their standard solutions in terms of molecular concentration were prepared. The solutions being thus prepared were poured in the small cup of the refractometer and the readings for the refractive index of the yellow line were taken ; the apparatus had been previously corrected for its zero error and a helium tube was excited by an induction coil to produce a continuous and prominent yellow ray for measuring the refractivities of the substances. Readings on the circular disc, which was graduated in degrees and minutes after zero error connection, gave the refractive value of the solution directly on consulting a table supplied by the manufacturers. The refractivity of the salts at several dilutions was thus determined and later on their molecular refractivity was calculated by multiplying the specific refractivity of the dissolved salt with the molecular weight. Specific refractivity was calculated by applying the Lorenz-Lorenz formula as appears in the text books.

FIG. 1.



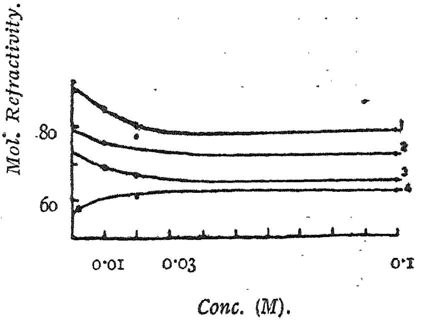
Curves 1—5 refer respectively to $K_4Cr(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_2Ni(CN)_4$ and $K_2Pd(CN)_4$.

FIG. 2.



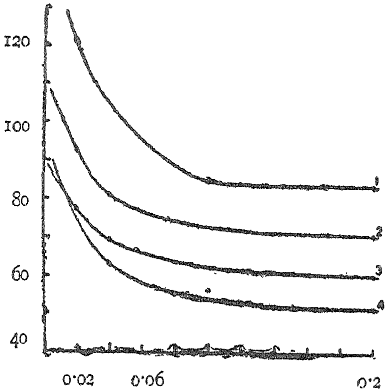
1—5 refer respectively to $K_4Fe(CN)_6$, $K_2Pt(CN)_4$ and KCN.

FIG. 3.



1—4 refer respectively to $K_4Os(CN)_6$, $K_4Ru(CN)_6$, $K_3Ir(CN)_6$ and $K_3Rh(CN)_6$.

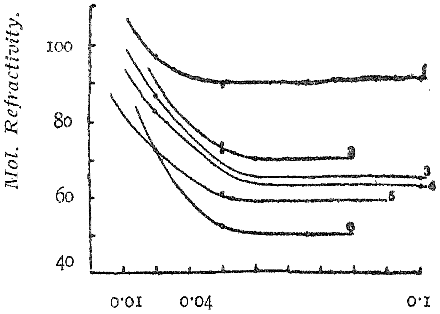
FIG. 4.



Conc. (M).

1—4 refer respectively to $[CoEn]_3Cl_3$, $[Co(NH_3)_6](NH_3)_3$, $[Co(NH_3)_5NO_3]Cl_2$ and $[Co(NH_3)_5Cl]SO_4$.

FIG 5.



Conc. (M).

1—6 refer respectively to $[Co\{C_2H_4(NH_2)_2\}_2Cl_2]Cl$, HCl, $2H_2O$; $[Co(NH_3)_4Br_2]Br$; $[Co(NH_3)_5NO_3](NO_3)_2$; $[Co(NH_3)_5Cl]Cl_2$; $[Co(NH_3)_5Cl]SeO_4$ and $[Co(NH_3)_5(SCN)]SeO_4$

Theory.

According to the electromagnetic theory of light both atoms and and ions experience an analogous polarisation in the homogeneous electric field waves. This action of light upon the atom is accompanied by a reaction of the atom on the light waves which cause a decrease in the velocity of their propagation, or in other words, the light ray is refracted. H. A. Lorenz has shown that there is a proportionality between the measure of polarisability of a particle and its molecular refractivity for long light waves and on the basis of theoretical considerations deduced the following expression for molecular refractivity

$$M.\,R. = \frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$$

where M is the molecular weight, n, the refractive index, and d, the density of the substance; and the specific refractivity, R_s of the solution is given by

$$\frac{n_s^2-1}{n_s^2+2}\cdot\frac{1}{d_s}$$

The specific refractivity of the salt in solution has been calculated from the formula, $100\, r_s = (r_w \times \%\ \text{water}) + (r_{\text{salt}} \times \%\ \text{salt})$, which when more elaborately expressed assumes the following forms,

$$R_{\text{salt}} = \frac{n_s^2-1}{n_s^2+2}\cdot\frac{1}{d_s}\cdot\frac{100}{P} - \left[\frac{n_w^2-1}{n_w^2+2}\cdot\frac{1}{d_w}\right]\frac{100-P}{P},$$

where n_s denotes the refractive index of the solution at the observed temperature, d_s, the density of the solution at the observed temp., P, percentage of the salt in the solution by weight, and n_w, d_w are the refractive index of water and density respectively at the observed temperature.

Molecular Refractivities of Complex Cyanides at 21°
under several Dilutions.

TABLE I.

Refractive index of distilled water at 21° = 1·3328.

Conc. of the soln.	Density of the soln.	Percentage strength of the soln.	Refractive index for yellow ray.	Refractivity		M. R_α.
				Specific.	Molecular.	
			$K_4Fe(CN)_6, 3H_2O$.			
M/11·5	1·0208	3·611	1·3391	0·171	62·11	62·1
M/57·5	1·0026	0·7347	1·3339	0·140	51·56	
M/115	1·0004	0·3682	1·3331	0·120	44·19	
			$K_2Pt(CN)_4$.			
M/10	1·0207	3·6978	1·3359	0·126	47·55	47·5
M/50	1·0023	0·7537	1·3333	0·120	45·30	
M/100	1·0005	0·3772	1·3329	0·090	33·97	
			$K_2Pd(CN)_4, 3H_2O$.			
M/10	1·0152	3·3783	1·3364	0·178	51·42	51·4
M/50	1·0016	0·6848	1·3337	0·170	49·12	
M/100	0·9999	0·3429	1·3334	0·140	40·45	
			KCN.			
M/10	1·0009	0·6540	1·3333	0·150	9·76	
M/50	0·9987	0·1303	1·3331	0·200	13·02	13·00
M/100	0·9985	0·0652	1·3330	0·200	13·02	

TABLE I (contd.).

Conc. of the soln.	Density of the soln.	Percentage strength of the soln.	Refractive index for yellow ray.	Refractivity		$\mathrm{M.\ R}_{\propto}$.
				Specific.	Molecular.	
			$K_3Fe(CN)_6$.			
M/10	1·0161	3·2403	1·3378	0·177	58·28	58·3
M/50	1·0018	0·6573	1·3340	0·170	55·97	
M/100	1·00002	0·3292	1·3335	0·160	52·67	
M/500	0·9986	0·0659	1·3330	0·100	32·92	
			$K_2Ni(CN)_4$.			
M/10	1·0112	2·3827	1·3381	0·213	51·32	
M/50	1·0008	0·4814	1·3336	0·220	53·00	53·00
M/100	0·9995	0·2410	1·3335	0·180	43·36	
M/500	0·9985	0·0482	1·3330	0·100	24·09	
			$K_3Co(CN)_6$.			
M/10	1·0177	3·6498	1·3378	0·170	56·47	56·5
M/50	1·0021	0·7413	1·3340	0·160	53·15	
M/100	1·0002	0·3714	1·3335	0·170	56·47	
M/500	0·9986	0·07439	1·3330	0·100	33·22	
			$K_4Cr(CN)_6$.			
M/10	1·0165	3·5854	1·3377	0·176	64·15	64·1
M/50	1·0019	0·7276	1·3339	0·170	61·96	
M/100	1·00006	0·3644	1·3335	0·170	61·96	
M/500	0·9985	0·07300	1·3329	0·100	36·45	

TABLE II.

Temperature = 27·4°.

			$K_3Rh(CN)_6$.			
M/10	1·0174	3·6980	1·33698	0·165	62·20	62·2
M/50	1·0004	0·7519	1·3327	0·162	60.96	
M/100	0·9983	0·3769	1·3323	0·175	65·85	
M/500	0·9966	0·0755	1·3318	0.155	58·32	
			$K_3Ir(CN)_6$.			
M/10	1·0267	4·543	1·3372	0·1394	65·03	65·0
M/50	1.0023	0·9309	1.33036	0·1435	66·94	
M/100	0·9992	0·4668	1·3324	0·147	68·57	
M/500	0·9968	0·0936	1·3319	0·145	67·64	

TABLE II (contd.).

Conc. of the soln.	Density of the soln.	Percentage str. of the solution.	Refractive index for yellow ray.	Refractivity Specific.	Refractivity Molecular.	M. R$_\infty$.
			$K_4Ru(CN)_6$.			
M/10	1·0241	4·572	1·3394	0·1734	71·81	71·8
M/50	1·0018	0·9346	1·3335	0·1870	77·45	
M/100	0·9990	0·4686	1·3326	0·1820	75·39	
M/500	0·9967	0·09396	1·3319	0·160	66·27	
			$K_4Os(CN)_6$.			
M/10	1·0341	5.391	1.3408	0·1564	78·72	78·7
M/50	1·0038	1·111	1·3336	0·1590	80·04	
M/100	0·9999	0.5573	1·3328	0·1680	84·57	
M/500	0·9969	0·1118	1·3319	0·1400	70·47	

Molecular Refractivities of Complex Cobalt Ammine Salts at 30°.

TABLE III.

Refractive index of distilled water at 30° determined by the refractometer = 1·3317 for yellow ray.

Conc. of the soln.	Density of the soln.	Percentage strength of the soln.	Refractive index for yellow ray.	Refractivity Specific.	Refractivity Molecular.	M.R$_\infty$
			$[Co\ En_3]Cl_3$.			
M/50	0·9985	0·6916	1·3331	0·241	83·26	83·3
M/100	0·9971	0·3463	1·3324	0·244	84·29	
M/250	0·9762	0·1387	1·3319	0·260	89·82	
M/500	0·9959	0·0693	1·3318	0·350	120·92	
			$[Co(NH_3)_6](NO_3)_3$.			
M/50	0·9992	0·6944	1·3329	0·203	70·43	70·4
M/250	0·9964	0·1393	1·3319	0·230	79·80	
M/500	0·9960	0·0696	1·3318	0·265	91·95	
			$[Co(NH_3)_5NO_3]Cl_2$.			
M/50	0·9988	0·5546	1·3329	0·216	59·81	59·8
M/250	0·9963	0·1112	1·3319	0·250	69·22	
M/500	0·9960	0·0556	1·3318	0·280	77·53	

TABLE III (contd.).

Conc. of the soln.	Density of the soln.	Percentage strength of the soln.	Refractive index for yellow ray.	Refractivity. Specific.	Refractivity. Molecular.	M. R_{∞}.
			$[Co(NH_3)_5NO_3]\ [NO_3]_2$.			
M/100	0·9974	0·3308	1·3322	0.196	64·67	64·7
M/250	0·9964	0·1325	1·3319	0·225	74·24	
M/500	0·9960	0·06626	1·3318	0·265	87·44	
			$[Co(NH_3)_5Cl]Cl_2$.			
M/100	0·9967	0·2513	1·3322	0·253	63·34	63·8
M/250	0·9961	0·1005	1·3319	0·290	72·60	
M/500	0·9959	0·0503	1·3318	0·330	82·60	
			$[Co(NH_3)_5Cl]SeO_4$.			
M/136·8	0·9973	0·3309	1·3321	0·182	58·72	58·7
M/250	0·9966	0·1813	1·33187	0·190	61·29	
M/500	0·9961	0·0907	1·3318	0·225	72·59	
			$[Co(NH_3)_5(SCN)]SeO_4$.			
M/150	0·9976	0·2305	1·3321	0·145	50·05	50·0
M/250	0·9968	0·1384	1·33187	0·150	51·77	
M/500	0·9962	0·06926	1·3318	0·210	72·48	
			$[Co(NH_3)_5Cl]SO_4$.			
M/50	0·9988	0·5535	1·3326	0·186	51·42	51·4
M/100	0·9972	0·2772	1·3322	0·202	55·84	
M/250	0·9963	0·11097	1·33187	0·230	63·58	
M/500	0·9960	0·05506	1·3318	0·280	77·40	
			$[Co(NH_3)_4SO_4]HSO_4$.			
M/100	0·9973	0·3379	1·33226	0·201	67·73	67·7
M/250	0·9963	0·1352	1·33187	0·220	74·13	
M/500	0·9960	0·06763	1·3318	0·270	90·98	
			$[Co(NH_3)_4(NO_2)_2]NO_3$.			
M/100	0·9971	0·2809	1·3322	0·209	58·72	
M/250	0·9962	0·1125	1·33187	0·250	70·24	
			$[Co(NH_3)_4(NO_2)_2]Cl$.			
M/20	1·0021	1·270	1·3344	0·222	56·48	56·5
M/50	0·9982	0·5098	1·3327	0·224	56·99	
M/100	0·9968	0·2552	1·3322	0·235	59·79	
M/250	0·9962	0·1021	1·33187	0·250	63·60	

TABLE III(contd.).

Conc. of he soln.	Density of the solution.	Percentage strength of soln.	Refractive index for yellow ray.	Refractivity Specific.	Refractivity Molecular.	$M.R_{\infty}$.
			$[Co(NH_3)_4(NO_2)_2](SeO_4)\frac{1}{2}$			
M/50	1·0004	0·7240	1·3326	0·148	53·60	53·60
M/100	0·9980	0·3629	1·3322	0·157	56·86	
M/250	0·9964	0·1454	1·3316	0·210	76·05	
M/500	0·9961	0·0727	1·3318	0·240	86·92	
			$[CO(NH_3)_4C_2O_4]Cl$.			
M/100	0·9967	0·2512	1·3321	0·227	56·84	
M/250	0·9961	0·1005	1·3318	0·230	57·59	
			$[Co(NH_3)_4Br_2]Br$.			
M/200	0·9967	0·1840	1·3319	0·190	69·68	69·5
M/250	0·9964	0·1472	1·33187	0·200	73.35	
M/500	0·9961	0·0736	1·3318	0·240	88·0	
			$[Co\{C_2H_4(NH_2)_2\}_2Cl_2]Cl, HCl, 2H_2O$.			
M/100	0·9972	0·3589	1·3325	0·254	90·88	90·9
M/250	0·9962	0·1436	1·3319	0·250	89·45	
M/500	0·9960	0·0718	1·3318	0·270	96·61	
			$[Co(NH_3)_4(H_2O)Cl]SeO_4$.			
M/150	0·9963	0·2166	1·3321	0·265	85·76	85·7
M/250	0·9960	0·1300	1·33187	0·270	87·38	
M/500	0·9958	0·0651	1·3318	0·310	100·32	
			$[Co(NH_3)_4CO_3]NO_3, \frac{1}{2} H_2O$.			
M/50	0·9979	0·5170	1·3325	0·212	54·69	54·7
M/100	0·9968	0·2588	1·3321	0·217	55·98	
M/250	0·9961	0·1036	1·3318	0·225	58·04	
			$[CO(NH_3)_4CO_3]Cl$.			
M/50	0·9972	0·4461	1·3325	0·245	54·49	54·5
M/100	0·9964	0·2232	1·3321	0·251	55·83	
M/250	0·9960	0·0893	1·33187	0·310	68·95	
M/500	0·9958	0·0446	1·3318	0·390	86·74	
			$[CO(NH_3)_4CO_3]_2SO_4, 3H_2O$.			
M/50	1·0014	1·046	1·3334	0·188	98·50	
M/100	0·9985	0·5247	1·3327	0·208	108·98	?
M/250	0·9968	0·2102	1·3320	0·208	108·98	
M/500	0·9962	0·1052	1·3318	0·210	110·03	
			$[CO(NH_3)_4CO_3]_2SeO_4, 3H_2O$.			
M/50	1·0021	1·1400	1·3335	0·185	105·66	
M/100	0·9989	0·5717	1·3327	0·194	110·80	?
M/250	0·9969	0·2291	1·3320	0·201	114·80	
M/500	0·9963	0·1146	1·3318	0·190	106·62	

DISCUSSION.

The foregoing tables show that the complex cyanogen salts may be classified into two main classes with regard to their behaviour towards refraction of light on progressive dilution of the salts.

(*i*) Some salts among those which have been investigated show a gradual diminution of molecular refractivity as the dilution of the solution is increased.

(*ii*) While others show a gradual rise in the value of their molecular refractivity with dilution. Compounds like potassium ferrocyanide, platinocyanide, palladocyanide, rhodicyanide, ferricyanide, nickelocyanide, and chromicyanide show a gradual fall in molecular refractivity with dilution, while potassiumiridi, rutheno, and osmo cyanides have a tendency to show an increase up to a certain dilution. It appears from this behaviour of the cyanides that the variation of refractivity is connected also with the stable or unstable nature of the complex among other plausible factors on which the refractivity of the salts depends in general, *e.g.*, ionisation, and molecular concentration,

FIG. 6.

$[Co(NH_3)_4CO_3]Cl$.

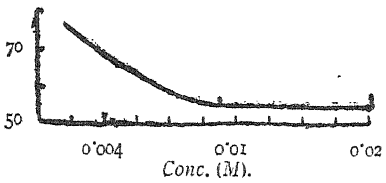
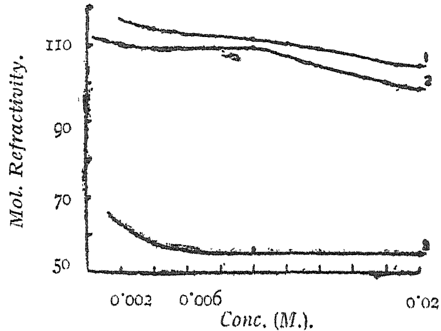
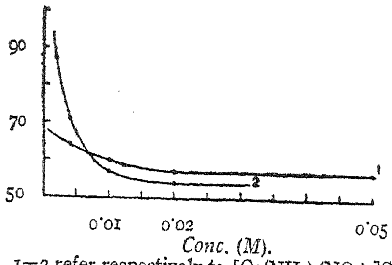


FIG. 7.



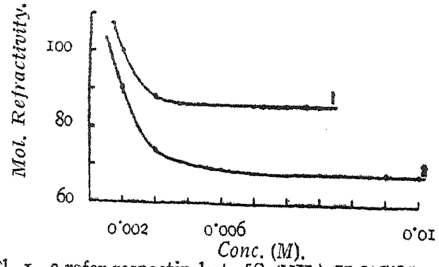
1—3 refer respectively to $[Co(NH_3)_4CO_3]_2SeO_4$, $3H_2O$; $[Co(NH_3)_4CO_3]_2$, SO_4, $3H_2O$; $[Co(NH_3)_4CO_3]NO_3$, $\frac{1}{2}$ H_2O

FIG. 8.



1—2 refer respectively to $[Co(NH_3)_4(NO_2)_2]Cl$ and $[Co(NH_3)_4(NO_2)_2](SeO_4)_{\frac{1}{2}}$.

FIG. 9.



1—2 refer respectively to $[Co(NH_3)_4(H_2O)Cl]SeO_4$ and $[Co(NH_3)_4\ SO_4]HSO_4$.

etc. The gradual diminution of molecular refractivity on dilution seems to be a normal behaviour of the complex salt, for with increasing dilution the intensity of the ionic field will be gradually weakened due to the progressive hydration of the heavily charged tervalent or quadrivalent complex ions. Dipole-water molecules under such conditions will form layers, masking the charged ions to a considerable extent which will result in correspondingly lowering the molecular refractivities of such complex salts under investigation. The gradual increase of molecular refractivity on dilutions seems to be an abnormal behaviour of the complex molecules and this may be ascribed to the gradual decomposition of the complex ions, into simpler ions whereby the electric field of the solution is intensified causing an increase in the molecular refractivity of the salts at a higher dilution. Complex iridium, ruthenium and osmium cyanides are of heavy metals and may, therefore, have a tendency to form comparatively less stable cyanide complexes than those of elements which are lighter; hence, the behaviour of the complex cyanides of these elements is opposite to that of other cyanides which appear in the tables.

Variation of the molecular refractivities of cobalt complex salts with dilution follow a more or less regular order. Almost all of these salts show a gradual increase of refractivity on dilution for which the instability of the cobalt complex radical seems to be responsible. In view of the above observations it may be further suggested that in the case of such complex salts as are comparatively less stable, the changes of molecular refractivity on dilution may furnish a suitable method for determining the degree of stability of the complex ion of the salt.

Molecular refractivities for red ray from an excited hydrogen tube were also observed, which presented rather anomalous variations with abrupt increase or decrease in the middle of the series of dilution. Such abrupt variations of a discontinuous nature suggest the possible formation of hydration compounds or decomposition of the complex salt.

Thanks are due to Dr. R. Samuel, Professor of Physics, Muslim University, Aligarh, for kindly furnishing me with the salts which have been investigated and allowing me to work in his laboratory for some time. My grateful thanks are also due to Prof. P. R. Ray of the Science College, Calcutta, for the interest he has taken in the discussion of the results published in this paper.

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Measurement of Molecular Areas of Cellulose from Different Sources by Surface Tension Method. Part II.

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Since the last decade vigorous attempts are being made by several investigators to determine the molecular size of cellulose. The older conception that cellulose consisted of a large number of anhydroglucose units, as first represented by the formula of Tollens, was modified some years ago by Hess, Karrer, Pringsheim and others who maintained that not more than four anhydroglucose units united by main valency bonds to form the cellulose molecule. The *X*-ray investigation, at the time, seemed to support this view. Staudinger, however, was the first to maintain from extensive investigation of both synthetic, and natural polymers that cellulose and similar substances consist of a very large number of anhydroglucose units united together to form a long chain thread-molecule whose length was about 1000 times the breadth or thickness. This view has since been corroborated by a large number of independent investigators working from different points of view. The improved method of *X*-ray investigation, hydrolysis of cellulose, the properties of the end-groups in the chain, all corroborate that cellulose is made up of a very large number of anhydroglucose units. There is, however, some essential difference as to the magnitude of the molecule and the number of anhydroglucose units that go to form the cellulose molecule. While Staudinger, as a result of his very careful viscosity measurements, maintains that cellulose molecule consists of some 750 anhydroglucose units, with molecular weight of about 120,000, other investigators, however, ascribe only 100-200 anhydroglucose units to the cellulose molecule. From *X*-ray investigations, Mark and Meyer (*Ber.*, 1928, **61**, 593) conclude that two glucose units, each of which is twisted 180° from its predecessor, go to form cellobiose units, as proposed by Haworth and about 60 such cellobiose units (*i.e.*, 120 anhydroglucose units) go to form one cellulose molecule. Some 40-50 of such molecules associate with each other somewhat loosely to form a micelle which is arranged parallel to the fibre-axis in the case of cotton. This order of magnitude finds corroboration in the work of Haworth (*Nature*, 1932, **129**, 365) who estimates tetramethylglucose obtained from the hydrolysis of methylated cellulose. This tetramethyl compound is evidently due to the non-reducing end-group of the open-chain. From this, the size of the molecule has been found to consist of about 120 anhydroglucose units. The other reducing end-group has been oxidised by Bergmann and Machemer (*Ber.*, 1930, **63**, 316) with hypoiodite solution and approximately the same order of magnitude has been obtained. This magnitude has also been corroborated by osmotic pressure measurements of cellulose solution by Buchner and Samwell (*Trans. Faraday Soc.*, 1933, **29**, 32) and also by the ultra-centrifuge measurements by Stamn (*J. Amer. Chem. Soc.*, 1930, **52**, 3047). Recently Craemer and Lansing (*Nature*, 1934, **133**, 870) report that ultra-centrifuge mesurements indicate a magnitude of 370-1110 glucose units in the cellulose molecule.

In the following experiments, an attempt has been made to determine the approximate order of magnitude of cellulose molecule by means of a method which has not so far been applied to it. It has been found that the surface tension of viscose solution changes with time and gradually attains a constant value after some time. This fall of surface tension is due (*cf.* Rideal, "Surface Chemistry," p. 31) to the molecules of the solute moving towards the surface where the concentration becomes greater than the bulk concentration and a unimolecular surface film is formed.

In this laboratory Ghosh and Nath (*J. Phys. Chem.*, 1932, **36**, 1916) studied the variation of surface tension of solutions of some complex organic substances, and modified the ring method of Freundlich with a view to avoid breaking up of the surface and cause the least possible disturbance. In the experiments to be described, this modified method has been followed for measuring surface tension.

The size of the cellulose molecule has been determined on the assumption that a unimolecular layer of cellulose molecule exists on the surface. Hence A, the area in sq. cm. per g. mole. $= 1/\tau$ where τ denotes excess concentration at surface and N, the Avogadro's number, τ can be calculated from the well known Gibb's equation

$$\tau = \frac{1}{RT} \quad \frac{d\sigma}{d \log c}$$

and may be found experimentally from the inclination of the curve obtained by plotting log of different concentrations against minimum surface tension ($d\sigma$).

The apparatus and procedure described by Ghosh and Nath (*loc. cit.*) has been followed for the purpose of measuring the surface tension.

Surface tension of the solution $= \sigma \times w_2/w_1$ where σ denotes surface tension of water at the temperature of the experiment. w_2 denotes the additional weight required to raise the basin from the surface of the solution while just touching, and w_1, the additional weight required to raise the basin from the surface of pure water.

EXPERIMENTAL.

The solution of viscose was made by the method described in Part I (Chowdhury and Bardhan, *J. Indian Chem. Soc*, 1936, **13**, 240), the only difference being that conductivity water was used in this case instead of distilled water. The glass vessels and the nickel basin were washed also with conductivity water and the basin was dried inside a desiccator containing strong sulphuric acid.

Surface tension was first measured about 5 minutes after the solution had been poured in the measuring vessel and then a series of readings were taken at an interval of about one hour. Tables I to III show the results obtained for the surface tension of pure water and of alkaline solutions of viscose determined at intervals *t* (in minutes) reckoned from the time at which the first observation was made. In the following tables *t* stands for time and σ for surface tension.

Variation of Surface Tension of Cotton-viscose Solution with Time at Different Concentrations at 20°.

TABLE I.

Composition of the solvent = 80% water, 4% of 16·91% NaOH soln. and 16% of 4·94% NaOH soln. Surface tension of water at 20° = 72·69 dynes/cm. Surface tension of the solvent at 20° = 55·67 dynes/cm.

Conc. = 0·002%.		Conc. = 0·004%.		Conc. = 0·006%.		Conc. = 0·01.		Conc. = 0·02%.	
t.	σ.	*t.*	σ.	*t.*	σ.	*t.*	σ.	*t.*	σ.
0	53·56	0	53·12	0	53·04	0	52·85	0	52·52
32	50·85	30	50·75	35	50·41	30	50·42	45	49·93
60	49·74	100	49·21	91	49·25	105	48·87	115	48·45
125	49·25	165	49·03	165	48·92	185	48·51	210	48·12
200	49·13	245	48·85	220	48·53	250	48·32	280	47·84
285	48·82	320	48·63	290	48·48	305	48·25	345	47·84
342	48·82	375	48·63	347	48·48	374	48·25	402	47·84
409	48·82	417	48·63	402	48·48	409	48·25		

Conc. =0·04%.		Conc. =0·06%.		Conc. =0·1%.		Conc. =0·14%.		Conc. =0·2%.	
t.	*σ*.	*t*.	*σ*.	*t*.	*σ*.	*t*.	*σ*.	*t*.	*σ*.
0	52·15	0	51·50	0	50·28	0	49·42	0	47·82
42	49·13	35	48·75	50	47·23	35	46·75	25	45·75
95	47·75	105	46·91	125	45·75	105	44·92	85	43·25
170	47·42	192	46·45	194	45·22	155	44·38	135	42·51
317	47·01	310	46·15	245	45·01	230	43·82	215	41·74
365	47·01	365	46·15	315	44·74	312	43·51	337	41·05
404	47·01	413	46·15	385	44·74	363	43·51	385	41·05
						415	43·51	425	41·05

Variation of Surface Tension of Jute-viscose Solution with Time at Different Concentrations at 20°.

TABLE II.

Composition and surface tension of solvent—same as before.

Conc. =0·002%.		Conc. =0·004%.		Conc. =0·006%.		Conc. =0·01%.		Conc. =0·02%.	
0	55·12	0	54·85	0	54·74	0	54·46	0	53·85
30	53·64	35	53·15	35	52·84	30	52·51	30	51·92
90	52·75	105	52·21	95	52·12	80	51·78	105	50·87
162	52·43	170	51·93	155	51·83	154	51·45	195	50·52
235	52·25	264	51·84	245	51·52	255	51·24	285	50·22
315	52·25	320	51·84	307	51·52	312	51·18	347	50·32
375	52·25	385	51·84	385	51·52	367	51·18	405	50·32
						403	51·18		

Conc. =0·04%.		Conc. =0·06%.		Conc. =0·1%.		Conc. =0·14%.		Conc. =0·2%.	
0	53·13	0	52·66	0	51·87	0	50·23	0	49·17
35	50·90	30	50·50	34	49·83	35	48·41	30	47·15
105	50·18	85	49·38	95	48·52	96	47·12	94	45·30
205	49·65	195	48·71	155	47·95	185	46·21	192	43·51
305	49·28	300	48·42	235	47·42	295	45·72	313	43·15
372	49·28	352	48·42	312	47·03	362	45·72	357	43·15
413	49·28	402	48·42	370	47·03	423	45·72	415	43·15
				415	47·03				

Variation of Surface Tension of Bamboo-viscose Solution with Time at Different Concentrations at 20°.

TABLE III.

Composition and surface tension of the solvent—same as before.

Conc. = 0·006%.		Conc. = 0·01%.		Conc. = 0·02%.		Conc. = 0·04%.	
t.	*σ.*	*t.*	*σ.*	*t.*	*σ.*	*t.*	*σ.*
0	55·42	0	55·23	0	54·97	0	54·24
30	54·25	35	54·82	30	53·45	35	52·21
95	53·86	105	53·25	94	52·48	115	51·32
165	53·75	195	53·21	185	51·91	195	50·95
205	53·72	270	52·74	280	51·58	290	50·53
270	53·52	325	52·74	347	51·58	364	50·53
345	53·52	397	52·74	405	51·58	424	50·53
402	53·52						
Conc. = 0·06%.		Conc. = 0·1%		Conc. = 0·14%		Conc. = 0·2%	
0	53·18	0	52·85	0	51·44	0	49·27
30	51·68	45	50·32	40	49·15	35	46·85
105	50·45	130	49·61	115	48·34	94	45·74
200	50·21	215	48·92	194	47·73	207	45·31
275	49·95	312	48·42	291	47·35	318	44·78
365	49·95	378	48·42	368	47·35	385	44·78
417	49·95	435	48·42	434	47·35	443	49·78

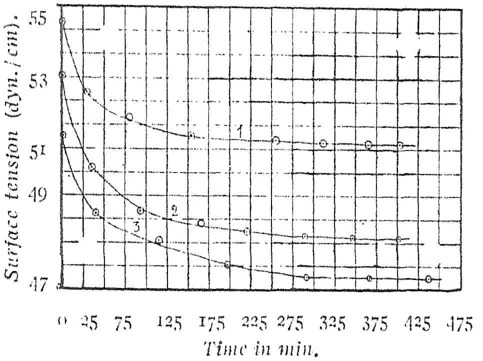
DISCUSSION.

Variation of Surface Tension with Time.

It will be seen from Fig. 1 that the variation of surface tension with time is fairly regular, unlike the behaviour of the colloidal dyestaff solution as observed by Ghosh and Nath (*loc. cit.*). Here the surface tension falls steadily though rapidly during the first 2 hours attaining a constant value after some 5 or 6 hours. The limiting surface tension can, therefore, be determined experimentally and need not be found by extrapolation from the curve.

FIG. 1.

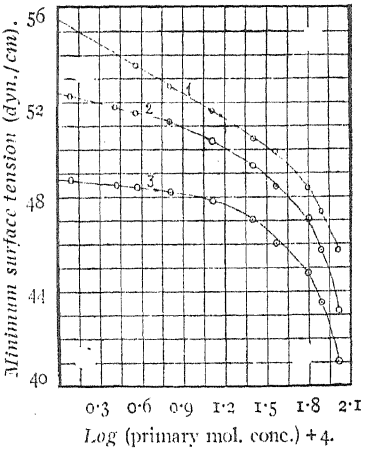
Viscose in NaOH *soln. at* 20°.



1—3 refer respectively to 0·01% jute, 0·006% cotton and 0·14% bamboo cellulose.

FIG. 2.

Viscose in NaOH *soln. at* 20°.



1—3 refer respectively to bamboo, jute and cotton cellulose.

Variation of Surface Tension with Concentration.

The values of the limiting surface tension of solutions of different concentrations are represented graphically in Fig. 2. It will be found that in very dilute solution the curve tends to become a straight line but the region of the concentrations in which such simple relationship of surface tension with concentrations is observed, is not, however, very great, as the curves bend rather quickly above the concentration 0·0081%, 0·01% and 0·24% in the case of cotton, jute and bamboo respectively. Attempts to correlate concentration and surface tension must, therefore, be limited to very low concentration. Gibb's equation is also applicable to solutions of high dilutions only, as the molecules are free to move only in very dilute solutions, where gas-laws are applicable. The molecular size of cellulose, particularly that of cotton cellulose, introduces, however, some complexities as such large molecules even in dilute solutions can not be absolutely without action on one another, though such action is naturally reduced to a minimum at very great dilutions. The values of τ are, therefore, determined from the inclinations of the above curves in high dilutions only. The molecular areas in sq. Å, as calculated from curve in Fig. 2, are given in Table IV. The standard celluloses from cotton, jute and bamboo, as used in viscosity measurements, were used in these experiments also. Calculation is based on ash and moisture free cellulose.

TABLE IV.

Substance.	$d\sigma/d \log c$.	Molecular area.
Cotton cellulose	0·49/0·7	571 sq. Å.
Jute cellulose	1·2/0·79	263·1
Bamboo cellulose	4·05/1·17	129·5

$$\tau = \frac{1}{RT} \cdot \frac{d\sigma}{d \log c} \text{ and } a = \text{ mol. area} = \frac{1}{\tau N} = \frac{RT}{N} \cdot \frac{d \log c}{d\sigma} \text{ sq. cm}$$

$$= \frac{8{\cdot}252 \times 10^7 \times 293}{6{\cdot}05 \times 10^{23}} \times \frac{0{\cdot}7}{0{\cdot}49} \times \frac{1}{10^{-16}} \text{ sq. Å} = 571 \text{ sq. Å}$$

It may be argued that the molecular area as calculated above, represents the area not of molecules but of micelle, as the molecules of cellulose might be associated with one another to form micelles in solution. Staudinger has, however, shown that cellulose in dilute solution forms molecule-colloids and does not tend to form micelles. This view has also been corroborated by X-ray investigation and also by N. K. Adam (*Trans. Faraday Soc.*, 1933, **29**, 105) who found in his spreading experiments that cellulose forms a monomolecular film, the thickness of which does not exceed that of an ordinary molecule. He also finds that the cellulose molecules lie absolutely flat on the water surface. It is, therefore, reasonable to assume that the films formed on the surface of the solutions investigated in this work, are also unimolecular in nature and the molecules lie flat on the surface. The area, as calculated, above, would, therefore, represent the average molecular size, provided the film on the surface is really unimolecular like the film investigated by Adam.

It is thus evident that the number of anhydroglucose groups in cellulose from different sources is not same and the degree of polymerisation varies according to the source from which cellulose is obtained. This view is also supported by the viscosity experiments as described in the previous part (*loc. cit.*).

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Use of Vanadous Sulphate as a Reducing Agent. Part II. Estimation of Chlorates, Nitrates and Persulphates.

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In a previous communication (Banerjee, *J. Indian Chem. Soc.*, 1935, **12**, 198) it has been stated that chlorates, nitrates and persulphates are reduced by vanadous sulphate. In the present paper it is shown that under certain conditions the reduction is quantitative and that each of the above substances may be volumetrically estimated with a fair degree of accuracy. The substances are reduced with an excess of the reagent which is then titrated back with a standard solution of potassium permanganate The vanadous salt is of course first standardised with the permanganate which oxidises it from divalent to the pentavalent state. With permanganate, the end-point is more sharp than with ferric alum and whenever the reduced product is without any action upon potassium permanganate, the latter should be preferred for back-titrations. An account of the preparation of the reagent and the general procedure for analysis have been given in Part I (*loc. cit.*).

EXPERIMENTAL.

Estimation of Chlorate.

Chlorates are not quantitatively reduced by vanadous sulphate at the ordinary temperature, but on boiling it is completely reduced to chloride

0·5836 G. of pure $NaClO_3$ was dissolved in water and the solution was made up to 250 c.c. A known volume of this solution was mixed with 10-15 c.c. of dilute sulphuric acid in a 150 c.c. flask from which air has been expelled by carbon dioxide. The mixture was reduced with a known amount of VSO_4 solution by boiling for about 5 minutes in a current of carbon dioxide. The solution was cooled, diluted with water and then titrated with 0·1*N*-$KMnO_4$ solution.

To test the method chlorate was also estimated from the solution by reducing with $FeSO_4$.

TABLE I.

VSO_4 soln. = 0·214N; $KMnO_4$ soln. = 0·1N. 1 c.c. of 0·1N-VSO_4 $= \frac{NaClO_3}{6 \times 10^4} = 0·001775$ g. of $NaClO_3$.

$NaClO_3$ soln.	VSO_4 soln.	$KMnO_4$ soln.	Amount of $NaClO_3$ found by VSO_4.	Amount of $NaClO_3$ found by $FeSO_4$.
10 c.c.	12 c.c.	12·5 c.c.	100·2%	99·6%
10	20	20·7	99·6	,,
10	13·5	13·55	100·1	,,
25	25	20·8	99·15	,,
25	25	20·7	99·8	,,
25	30	31·3	100·2	,,

Estimation of Nitrate.

The reaction between nitric acid and vanadous sulphate is far more complex than with chlorate or persulphate. It depends upon the relative concentrations of the reacting substances and temperature. It has been found that at ordinary temperature nitric oxide is formed when vanadium salt is slowly added to a moderately strong nitric acid solution. On the other hand, when the nitric acid is added to an excess of vanadous sulphate, no nitric oxide comes out. Probably the nitric oxide is absorbed by the excess of vanadous sulphate and remains in solution (*cf.* Friend, "Text Book of Inorganic Chemistry"). If however the nitric acid or a nitrate be added to a large excess of vanadous salt containing sufficient sulphuric acid and the mixture boiled in a current of carbon dioxide, the nitric acid is completely reduced to ammonia. Under these conditions by reducing to ammonia nitric acid can be estimated.

0·3211 G. of KNO_3 was dissolved in water and the solution was made up to 250 c.c.; 2 to 3 c.c. of H_2SO_4 (conc.) diluted with 25 c.c. of water were saturated with carbon dioxide in a 150 c.c. flask. A known volume of the VSO_4 solution was run into the flask from the burette and the KNO_3 solution was then added. The mixture was heated to boiling and kept at this temperature for about 5 minutes in a current of carbon dioxide. The solution was then cooled and titrated with the standard solution of $KMnO_4$. The VSO_4 solution was always freshly standardised under similar conditions so that any error due to impurities present in sulphuric acid or water might be eliminated.

TABLE II.

VSO_4 soln. = 0·2125N ; $KMnO_4$ soln. = 0·1N. 1 C.c. of 0·1N-VSO_4 soln. = $\frac{KNO_3}{8 \times 10^4}$ = 0·00126375 g. of KNO_3.

KNO_3 soln.	VSO_4 soln.	$KMnO_4$ soln.	KNO_3 found
5·0 c.c.	10 c.c.	16·20 c.c.	99·4%
10	20	32·35	99·8
10	20	32·40	99·4
10	25	43·00	99·6
15	30	48·65	99·1
15	20	27·30	99·7

Estimation of Persulphate.

Persulphuric acid is not completely reduced by vanadous salt either in the cold or when hot. If, however, it is treated with an excess of vanadous salt in the presence of a ferric salt, the per-acid is completely reduced to sulphate even at the ordinary temperature. Ferric salt is probably first reduced to ferrous salt which then acts on the persulphuric acid. The reactions may be represented by the following equations :

$$2Fe^{+++} + V^{++} = 2Fe^{+++}V^{++++}$$

On adding, $$\begin{array}{l} S_2O_8'' + 2Fe^{++} = 2SO_4'' + 2Fe^{+++} \\ \hline S_2O_8'' + V^{++} = 2SO_4'' + V^{++++} \end{array}$$

At the end of the reaction, the ferric iron will be in the ferrous state if there is enough V^{++} present in the solution. A part of the persulphuric is also directly reduced by vanadous salt. It is evident from the above equations that a small amount of Fe^{+++} is sufficient for the process of reduction to go on until all the persulphuric acid is reduced. To test this point experiments were carried out to find the minimum quantity of ferric salt that must be added to complete the reaction and it was found that 8 to 10 drops of a 0·1N ferric alum solution were necessary for this purpose.

5·5933 G. of Merck's (G.R.) ammonium persulphate were dissolved in 500 c.c. of water. A known volume of this solution was taken in a 150 c.c. flask from which air has been removed by a stream of carbon dioxide. A few c.c. of ferric alum solution were added and then a known volume of VSO_4 solution was run into the flask; 15 to 20 c.c. of H_2SO_4 were added and the mixture was allowed to stand for 2-3 minutes in a current of carbon dioxide. The solution was then titrated with the standard $KMnO_4$ solution.

To test the results the persulphuric acid was also estimated by reducing with ferrous sulphate.

TABLE III.

$VSO_4 = 0{\cdot}214N$; $KMnO_4$ soln. $= 0{\cdot}1N$; Ferric alum soln. $= 0{\cdot}1N$.

$$1\text{ C.c. of } 0{\cdot}1N\text{-}VSO_4\text{soln.} = \frac{(NH_4)_2S_2O_8}{2\times10^4} = 0{\cdot}01141\text{g. of }(NH_4)_2S_2O_8.$$

Persulphate soln.	Ferric alum soln.	VSO_4 soln.	$KMnO_4$ soln.	Amount of persulphate found by	
				VSO_4.	$FeSO_4$.
10 c.c.	2 c.c.	10.0 c.c.	11·65 c.c.	99·5%	99·32%
10	5	10·1	11·0	99·1	,,
10	1	10·0	11·7	99·0	,,
25	10	25·0	29·2	99·15	,,
25	2	20·0	18.4	99·55	,,
25	1	25·5	30·25	99·2	,,

SUMMARY.

1. Chlorates, nitrates and persulphates may be estimated by introducing a known quantity into an excess of vanadous sulphate solution and titrating back the excess with a standard solution of potassium permanganate.

2. Chlorates and nitrates are reduced by vanadous sulphate to chlorides and ammonia respectively by boiling in presence of sulphuric acid in a current of carbon dioxide. In the case of persulphate the reduction is complete only in the presence of a little ferric salt.

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Studies in Organo-Arsenic Compounds. Part III.

BY HIRENDRA NATH DAS-GUPTA.

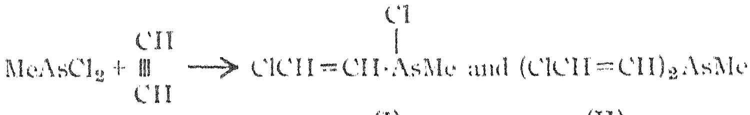
The action of ethylene and acetylene upon chlorides of sulphur, arsenic, antimony and tin has been studied by numerous investigators. Defert (*Monatsh.*, 1919, **40**, 313) obtained a compound by reacting acetylene with arsenic trichloride in the presence of aluminium chloride to which he incorrectly assigned the formula $AsCl_3, 2C_2H_2$. The systematic study of the nature of the reaction products was done by Green and Price (*J. Chem. Soc.*, 1921, **119**, 448) who showed that three substances of novel types are produced in this reaction, *viz.*, β-Chlorovinyldichloroarsine ($Cl{\cdot}CH = CH{\cdot}AsCl_2$) ; $\beta\beta'$ - dichlorodivinylchloroarsine [$(Cl{\cdot}CH{=}CH)_2AsCl$] and $\beta\beta'\beta''$-trichlorotrivinylarsine [$(Cl{\cdot}CH{=}CH)_3As$]. The results obtained have been confirmed by Mann and Pope (*J. Chem. Soc.*, 1922, **121**, 1754). Lewis and Stiegler (*J. Amer. Chem. Soc.*, 1925, **47**, 2546) have proved conclusively that the above types of reactions can easily be extended to bromo and iodo derivatives of arsenic. A survey of the literature thus shows that

(*a*) Acetylene is readily absorbed by halogenated trivalent arsenic derivatives in presence of anhydrous aluminium chloride.

(*b*) The formation of the different arsines takes place in stages and that with continued bubbling of the gas through the reaction mixture with corresponding diminished temperature, the yield of tertiary arsine increases at the cost of the primary one. If, however, the supply of the gas be stopped after a definite period and the temperature be allowed to increase the yield of the primary arsine increases with corresponding decrease in the proportion of the tertiary arsine till the equilibrium is established.

(*c*) The halogen attached to β-carbon, containing a double bond, possesses the characteristic stability.

The study of the literature lends strong support to the view that methyl arsenious chloride, in which the arsenic is in the trivalent state and contains chlorine as well, would behave similarly. The present paper describes the action of acetylene on methyl arsenious chloride and as expected two different types of compounds *viz.*, β-chlorovinyl methylchloroarsine (I) and ββ′-dichlorodivinyl methylarsine (II) have now been isolated. ββ′-Dichlorodivinyl methylarsine has been identified by the formation of identical derivatives (*vide* experimental) of the compound prepared by Lewis and Stiegler (*loc. cit.*) from *bis*-β-chlorovinylchloroarsine. The reactions take place in the following way :—



$$\mathrm{MeAsCl_2} + \begin{matrix}\mathrm{CH}\\ \parallel\!| \\ \mathrm{CH}\end{matrix} \longrightarrow \mathrm{ClCH{=}CH\cdot}\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{As}}\mathrm{Me} \text{ and } \mathrm{(ClCH{=}CH)_2AsMe}$$

(I) (II)

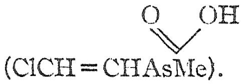
The behaviour of the chlorine atom attached to the arsenic is analogous to that of other chlorovinyl compounds as it readily gives derivatives like oxide, arsinic acid, sulphide, cyanide, mixed arsine, arsonium compounds, double salt, etc. These compounds are less irritant to the mucous membrane of the nose than the chlorovinyl compounds.

These experiments are in agreement with the fact that acetylene reacts with phenyl arsenious chloride in presence of aluminium chloride and yields two types of compounds, *viz.* $\mathrm{Ph.}\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{As}}\mathrm{CH{=}CHCl}$ and $\mathrm{Ph{\cdot}As\ (CH{=}CHCl)_2}$ (Das-Gupta, *J. Indian. Chem. Soc.*, 1935, **12**, 627).

EXPERIMENTAL.

β-Chlorovinylmethylchloroarsine (I).—Acetylene, washed through saturated solution of sodium bisulphite and dried by concentrated sulphuric acid, was passed for 2 hours through a mixture of methyl dichloroarsine (50 g.) and anhydrous aluminium chloride (20 g.) at 10−15°. The mixture was well stirred throughout and stirring continued for 8 hours more, the temp. not rising above 25°. The brown viscous liquid was decomposed in the cold by 20% hydrochloric acid. The lower thick brown layer was removed, repeatedly washed with dilute hydrochloric acid and extracted with ether. The ethereal solution was dried over calcium chloride, the ether removed and the brown oil was fractionated at 10 mm. Three fractions were collected: (*i*) at 45−65°, a colourless oil consisting of a mixture of unchanged original compound and other by-products. (*ii*) at 110−15°, consisting of the bulk of the desired product (iii) at 140−45°, the tertiary arsine. The second fraction was redistilled at 112-15°/10 mm.

It is colourless when freshly distilled but on storage it slowly turns pink. It does not attack the nose so intensively as the parent substance but it produces blister on the skin which takes a long time to heal up. [Found : Cl, 37·2 ; As, 39·95 ; M.W. (cryoscopic), 184·3, 186·1. $C_3H_5Cl_2As$ requires Cl, 37·9 ; As, 40·1 per cent. M. W. 187].



β-Chlorovinylmethylarsinic Acid ($\mathrm{ClCH{=}CH}\overset{\mathrm{O}\quad\mathrm{OH}}{\overset{\diagdown\diagup}{\mathrm{As}}}\mathrm{Me}$).

β-Chlorovinylmethylchloroarsine (1 g.) was suspended in water (3 c.c.) and treated with excess of perhydrol. Within a short time a vigorous reaction ensued with rise in temperature. The mixture was heated for some time on water-bath with occasional addition of fresh perhydrol till the oil was all dissolved. The pasty residue was cooled in ice and extracted with a mixture of acetone and ether (1 : 1), colourless crystals of the arsinic acid separated on spontaneous evaporation of the solution. It was recrystallised from acetone, m. p. 149-150° (uncorr.). (Found : Cl, 19·1 ; As, 40·5 : $C_3H_6O_2$ ClAs requires Cl, 19·2 ; As, 40·6 per cent).

β-Chlorovinylmethylarsenious Sulphide.

$$(\mathrm{ClCH{=}CH}\underset{\mathrm{Me}}{\underset{|}{\mathrm{As}}}\cdot\mathrm{S}\cdot\underset{\mathrm{Me}}{\underset{|}{\mathrm{As}}}\mathrm{CH{=}CHCl})$$

It was obtained by passing sulphuretted hydrogen through an alcoholic solution of (I) for 1 hour. The solution was filtered from minute traces of yellow precipitate and the filtrate was diluted with water and the oil obtained was washed with water and dried in a vacuum desiccator for 2 days. It is light yellow in colour and is soluble in most of the common organic solvents. (Found : Cl, 20·8 ; As, 44·6. $C_6H_{10}Cl_2As_2S$ requires Cl, 21·19 ; As, 44·7 per cent).

β-Chlorovinylmethylarsenious Cyanide [ClCH=CHAs(CN)Me].—An alcoholic solution of (I) was treated with an aqueous solution of potassium cyanide, when potassium chloride separated with considerable rise in temperature. The filtrate on cooling and dilution with water gave a light yellow oil, which was separated, repeatedly washed with water and then dried in vacuo. (Found : Cl, 20·5 ; As, 42·1. C_4H_5NClAs requires Cl, 20·0 ; As, 42·2 per cent).

β-Chlorovinylmethylarsenious Oxide ($ClCH:CHAs\cdot O\cdot AsCH=CHCl$).—An alcoholic solution of (I) was added to an alcoholic solution of sodium ethoxide when sodium chloride was precipitated. The filtered solution was concentrated, cooled and treated with ether, when silky needles were obtained which were crystallised twice from water and finally from alcohol. (Found : Cl. 22·1 ; As, 47·2. $C_6H_{10}OCl_2As_2$, requires Cl, 22·2 ; As, 47·02 per cent).

β-Chlorovinylmethylphenylarsine ($ClCH=CHAs\ (Me)\ C_6H_5$).—To the ethereal solution of the Grignard reagent from bromobenzene (5 g.), magnesium (0·8 g.), β-chlorovinyl methylchloroarsine (6 g.) in absolute ether was added drop by drop with stirring. On keeping overnight the mixture was decomposed by ice cold water and the resulting product was extracted with ether, the ethereal solution dried by calcium chloride and the compound was purified by reprecipitating it several times from ether by alcohol. (Found : Cl, 15·4 ; As, 32·1. $C_9H_{10}ClAs$ requires Cl, 15·5 ; As, 32·8 per cent).

ββ-dichlorovinylmethylarsine (II).—It was obtained in a crude condition in the fraction 140-45°/10 mm. after passing acetylene through methylarsenius chloride (*vide supra*). The oil was repeatedly washed with dilute acid and water, dried and redistilled. It was identified by preparing mercuric chloride double compound $[Cl\cdot CH=CH)_2\ As\ Me,\ Hg\ Cl_2]$, m. p. and mixed m. p. with Lewis and Stiegler's comp. 162°. (Found : As, 15·5. $C_5H_7\ Cl_4\ As\ Hg$ requires As, 15·4 per cent); and also the arsonium iodide, m. p. and mixed m. p. 243° (decomp.). (Found : As, 21·1. $C_6H_{10}Cl_2I\ As$ requires As, 21·1 per cent). (*cf.* Lewis and Stiegler, *loc. cit.*)

This compound was also prepared from β-chlorovinyl methylchloroarsine and acetylene in presence of aluminium chloride at a temperature of 5-10° and distilling the resulting product. (Found : As, 35·3. $C_5H_7Cl_2As$ requires As, 35·2 per cent).

My grateful thanks are due to Dr. M. Goswami for his keen interest and for placing all the resources of his laboratory at my disposal and to Prof. Dr. H. K. Sen and Mr. B. C. Ray for their kind encouragements.

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Studies in the Coagulation of Colloids. Part XII. "Zonal effect" in the Change of Refractivity during Mutual Coagulations.

By Shridhar Sarvottam Joshi and K. P. N. Panikkar.

In Part X of this series (Joshi and Panikkar, *J. Indian Chem. Soc.*, 1934, **11**, 797; also *J. chim. Phys.*, 1935, **32**, 455) results were given for the change of viscosity during a number of *mutual* coagulations between oppositely charged sols. Subsequent work in Part XI (Joshi and Jaya Rao, *J. Indian Chem. Soc.*, 1936, **13**, 141) on the variation of μ, the refractive index of a number of coagulating systems showed that this property is sufficiently sensitive and can be employed with convenience in order to follow the course of a coagulation. In the literature of the subject, *mutual* coagulations have been but scantily examined in respect of their kinetics. It was of interest, therefore, to study these by use of this new method, *viz.*, change of refractivity.

Experimental.

The colloidal solutions of manganese dioxide, arsenious sulphide and ferric oxide were prepared and estimated for their colloid contents as described in Part X (*loc. cit.*). The last quantities were respectively 2·1 g. of MnO_2, 3·0 g. of As_2S_3 and 1·5 g. of Fe_2O_3 per litre. The general procedure, precautions as to constancy of temperature etc., and the observation of changes in μ are described in Part XI (*loc. cit.*). In experiments corresponding to curves No. 1 to 4 varying amounts of the As_2S_3 sol were diluted with water to 1 c.c., and mixed in the refractometer cell with an equal volume of the Fe_2O_3 sol at a known time, the two sols having been pre-heated to 35°. Curve 5 relates to the use of colloid MnO_2 instead of colloid As_2S_3. These results are shown in Table I, and partly by μ—time curves in Fig. 1.

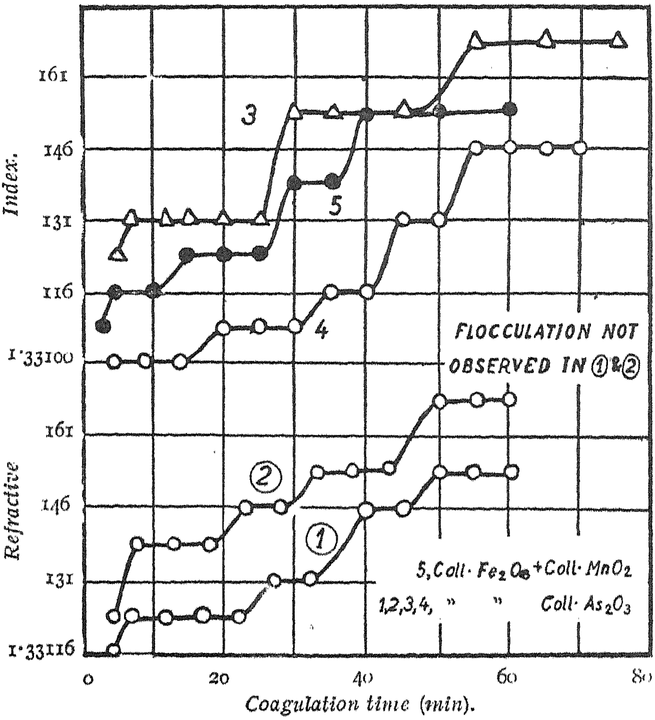
Table I.

Amounts of the sols.	Curve No.	Remarks.
1 C.c. Fe_2O_3 + 1 c.c. As_2S_3 + 0·0 c.c. H_2O	1	No flocculation in first 60 mins.
+ 0·5 ,, + 0·5 ,,	2	No flocculation.
+ 0·2 ,, + 0·8 ,,	3	Flocculation after 65 mins.
+ 0·1 ,, + 0·9 ,,	4	Copious flocculation after 70 mins.
+ 0·25 c.c. MnO_2 + 0·75	5	Complete coagulation in about 60 mins.
+ 1 ,, + 0	Not shown	No flocculation.

DISCUSSION

It is seen from these results that the occurrence of discontinuities is as conspicuous in these *mutual* as in the electrolytic coagulations reported earlier in Part XI (*loc. cit.*). Further support to this conclusion has been obtained recently in these laboratories in the variation of the transparency of coagulating sols. These results will be published shortly. It may, therefore, be generalised that this *zonal effect* is almost a characteristic of the act of coagulation. The problem next to be investigated would, appear therefore, to be the elucidation of factors whose operation suppresses or marks the occurrence of the *zonal effect* in rapid coagulations.

FIG. 1.



In work in this series, as is usually the practice in studies of coagulation kinetics, record of the progress of the change was discontinued as soon as the system became appreciably heterogeneous by the production of flocculi. This is the principal source oft he not too well defined a term, *turbidity*, so familiar in coagulation effects. Now an interesting observation was made that the coagulation-time curves, corresponding (*i*) to the incipience of flocculation and turbidity (curves No. 3, 4, 5) and (*ii*) when these effects were unnoticed (curves 1, 2), belonged essentially to the same family of curves, all characterised by a similar and marked *zonal effect*. Precisely similar observations were made in a number of μ-time curves for coagulation in which the proportion of colloid MnO_2 was varied from 0·2 to 1·0 c.c. mixed (after dilution with water in each case to 1·0 c.c. with 1 c.c. of colloid Fe_2O_3. Since these curves did not show any additional features, only one of them (curve 5) is shown in Fig. 1. Analogous results were obtained earlier (Part XI, *loc. cit.*; *cf.* also Joshi and Panikkar, *Proc. Acad. Sci. U.P.*, *loc. cit.* also, *J. chim. Phys.*, *loc. cit.*) in the finding that marked changes of viscosity occurred independently of whether the corresponding mixture showed flocculation effect such as the familiar rise in turbidity.

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Studies in the Coagulation of Colloids. Part XIII. "Zonal effect" in the Opacity Changes in the Coagulation of Colloid Manganese Dioxide.

BY SHRIDHAR SARVOTTAM JOSHI AND S. JAYA RAO.

In Parts XI and XII of this series (*J. Indian Chem. Soc.*, 1936, **13**, 141, 309; *cf.* also, *Current Science*, 1936, **4**, 481), it was observed that the change of the refractive index of the above sol during any one of its numerous electrolytic and mutual coagulations examined showed an unmistakable and characteristic '*zonal effect*,' which became more conspicuous, the *slower* the change. The present paper records observations of this effect, it would appear for the first time in the field of coagulation kinetics, in the change of the *opacity* during coagulation.

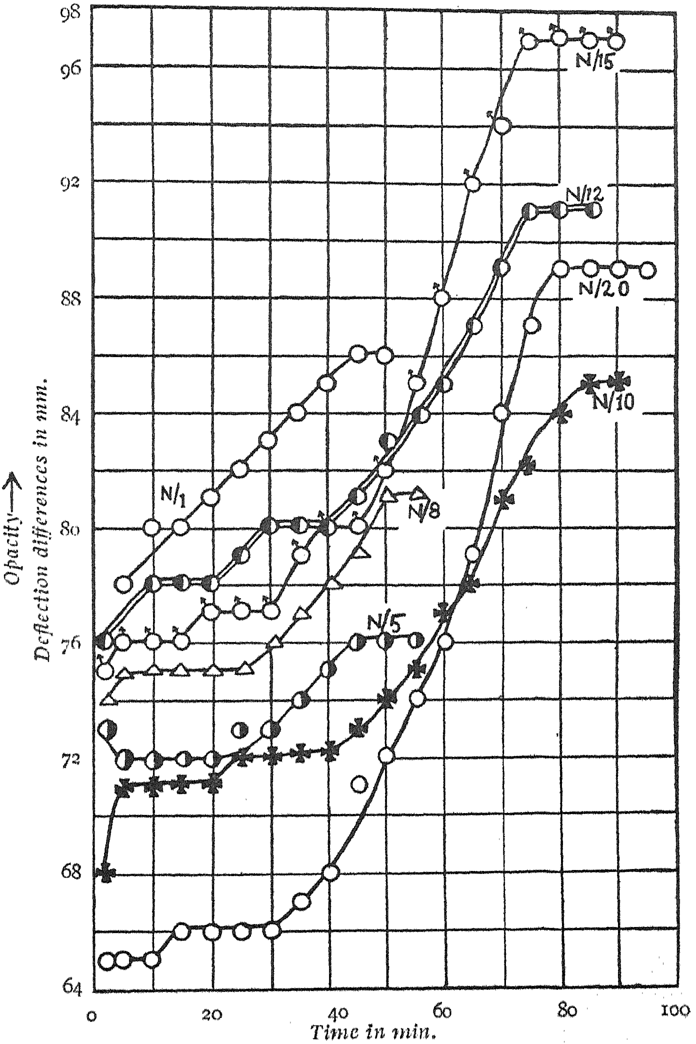
EXPERIMENTAL.

The colloid was prepared and its strength estimated. *viz*, 1·85 g. MnO_2 per litre, as in Part XI (*loc. cit.*). The opacity during coagulation was measured by use of a sensitive thermopile and a low resistance Broca galvanometer (*cf.* Mukherjee and Majumdar, *J. Chem. Soc.*, 1924, **125**, 757). Light from a 4-volt lamp run at a constant potential from a battery of storage cells was first passed through distilled water in an optical cell in order to eliminate the heat radiation and then allowed to fall on the cell with optically flat surfaces, which contained the coagulating mixture. Intensity of the light transmitted by the sol was indicated by the deflections of the galvanometer. The source of light, the water-filter, the coagulating sol and the thermopile were enclosed in an air thermostat with glass sides. This was almost wholly immersed in water contained in another thermostat with glass sides, except on the top, which was closed by a well fitting cover insulated against heat conduction by thick pads of sheep wool. The outer thermostat was also well covered with pads of wool except on the glass faces which were suitably covered to screen off any stray light. The temperature of this thermostat was kept constant at 23·5±5°. Under these conditions the thermopile was found to be well protected against any external radiation and changes of temperature. The galvanometer deflection for the colloid, diluted with an equal amount of water, was found to be 249 mm. When the same amount of the colloid was mixed with an equal volume of a solution of the coagulant employed, *viz.*, potassium chloride, the galvanometer deflection was smaller. The difference of these two deflections was taken as a measure of the opacity of the coagulating sol. These measurements were continued, till it was suspected that the system had become heterogeneous by formation of discrete particles of the coagulum. The seven curves in Fig. 1 show the variation of opacity during coagulations due to solutions of potassium chloride whose concentration before admixture with the sol was varied in the range $N/1$ to $N/20$.

DISCUSSION.

These results show that while on the whole, the opacity of the colloid increased during coagulation, the rate of its increase by increasing the electrolyte concentration was not marked. Substantially similar results were obtained in Part XI in observations of the changes of refractivity during coagulation. The chief feature of interest of the coagulation-time curves now reported is in the discontinuous or *zonal* variation of opacity, in confirmation of earlier results obtained with viscosity and refractivity measurements. Variation of opacity has been amongst the earliest and widest used properties in the kinetics of coagulation. The observation of the *zonal effect* using such an approved property, therefore, supports the deduction made in Part XII that presumably, the *zonal effect* inheres in the mechanism of coagulation. In agreement with earlier results (Part XI) the opacity-time

FIG. 1.



curves in Fig. 1 show that the *zonal effect* is practically absent in *rapid* coagulations (*cf.* curves for $N/1$-KCl), and that the number of *zones* and (in the majority of cases) the duration of each *zone* tends to increase by increasing the dilution of the coagulant, *i.e.*, the slower the change. Although a complete theory of the opacity of a coagulating colloid is not available in the literature, it can be anticipated on general considerations, that the (*a*) effective particle-size and *difference* in the refractive index for the particles and the dispersion medium are its chief determinants. Now, while considerable evidence is afforded by results in Parts XI and XII that at any rate the over-all refractivity of the sol varies *zonally* during coagulation, nothing definite can be stated about changes in the refractive index characteristic of (*b*) the particles and (*c*) the medium. (*b*) would appear to depend upon the refractivity for the dispersed material in its pure state, the extent of its hydration, the nature and the amount of the electrolytic material associated with the "*double layer*" and especially its electrical condition. (*c*) is not expected to change sensibly. The difference between (*b*) and (*c*), however, is significant and may vary appreciably. More experimental data are, however, needed at the present stage in the general theoretical development of the subject in order to envisage the observed *zonal* variation of opacity in terms of (*a*) (*b*) and (*c*).

The foregoing results have some interest in regard to the suggestion made by numerous workers (*cf.* Freundlich, "Colloid and Capillary Chemistry," 1926, pp. 424-450; also, Desai, *Trans. Faraday Soc.*, 1928, **24**, 191) that coagulation is *autocatalytic*. Evidence has been adduced in previous papers in this series (Parts V-IX, *J. Indian Chem. Soc.*, 1924-36) that autocatalysis can not be a *general* characteristic of coagulation. Now, the curves in Fig. 1 show that the horizontal *zones* are produced more frequently during the earlier stages of coagulation and that this tendency increases with the dilution of the coagulant. These conditions are favourable for autocatalysis as shown by the so-called **S**-shaped curves. It may be suggested, therefore, that the evidence for *autocatalysis* might arise from the presence of these *zones of coagulation* during which the property selected for measuring coagulation is not sensibly affected, and whose combined effect gives the initial section of the coagulation-time curve its low gradient.

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Analytical Uses of Nessler's Reagent. Quantitative Estimation of Monosaccharides and Disaccharides. Estimation of Furfural. Part II.

By M. Goswami and B. C. Das-Purkaystha.

It has been shown by one of us in a previous paper (*J. Indian Chem. Soc.*, 1935, **12**, 714) that Nessler's reagent can be used successfully to distinguish ketones from aldehydes, all of which latter reduce it, the only exception being *o*-hydroxy-aldehydes and hydroxy-ketones which show anomaly that can be otherwise explained. It has also been shown that by raplacing sodium hydoxide by sodium carbonate, glucose can be directly estimated quantitatively without recourse to an intermediate standard. This method has now been extended for the estimation of other monosaccharides and disaccharides. A preliminary note on the estimation of fructose and cane sugar has already been published (*J. Indian Chem. Soc.*, 1936, **13**, 73).

The reaction between glucose and K_2HgI_4 is evidently one of reduction of the latter first to Hg_2I_2 and thence to metallic Hg as follows :—

$$2K_2HgI_4 \rightarrow 4KI + Hg2I_2 + I_2 \rightarrow 2KI + K_2Hg\,I_4 + Hg + I_2$$

This liberated I_2 corresponding to one mercury and one oxygen atom is utilised to oxidise glucose. The principle of the method is based on the estimation of the liberated mercury, the amount of which denotes the degree of reducibility of glucose. It has been shown that under the standard conditions prescribed, one glucose molecule takes up two atoms of oxygen *i.e.*, liberates two atoms of mercury. It was also indicated that the reducibility of fructose proceeds further than that of glucose. This has now been established. It has been found that under the standard conditions prescribed the following are the respective proportions of oxygen which are utilised to oxidise the principal mono- and disaccharides

1 mol.	Arabinose	...	1 atom of oxygen.	Table I
	Glucose	...	2 atoms	
2	Fructose	...	5	II and III
2	Canesugar	...	9	IV
2	Lactose	...	5	V
2	Maltose	...	5	VI

In the case of furfural sodium hydroxide has been used instead of sodium carbonate which gives low results and it has been found that in this case one molecule requires one atom of oxygen (Table VII).

For the purpose of standardising our method we have taken 'Difco' and 'Analar' standard of sugars and Kahlbaum's purest sugars for calorimetric estimations. Before preparing the solutions the sugars have been dried in *vacuo* at 80−90° for 1 hour. The melting points were then checked. We have reasons to think that even with such precautions we were unable to get 100% pure sugars and this will perhaps explain the slight variations from the theoretical values.

It was thought worth while to extend the method to estimate minute quantities of glucose (0·1 g. in 100 c. c.) using very small quantities of reagents. Table VIII will show that the results are satisfactory. This micro-estimation was then extended to the determinations of sugar in blood. Tables IX and X will show that this new micro-estimation method compares very favourably with the other recognised methods of which no two methods give identical results even for the same sample of blood.*

Further applications of Nessler's reagent for the quantitative estimation of (aromatic and aliphatic) aldehydes (saturated and olefinic) are in progress.

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* Quantitative Clinical Chemistry by Peters and Van Slyke, Vol. II, p. 455 and *J. Biol. Chem.*, 1929, **83**, 51.

	Miligram of sugar for 100 c. c. of blood compared with that by Benedict's method taken as 100.		
	Average.	Maximum.	Minimum.
Method Shaffer-Hartmana Somogyi-copper titration method. *J. Biol. Chem.*, 1926, **70**, 599	121	149	109
Folin Ferricyanide colorimetric method. *J. Biol. Chem.*, 1928, **77**, 421 ; 1929, **81**, 231	98	124	86
Van Slyke Hawkine Ferricyanide gasometric and timing method. *J. Biol. Chem.*, 1929, **84**, 69; 1929, **83**, 51 ...	120	138	115

EXPERIMENTAL.

Potassium mercuric iodide used in the following experiments had the following composition :

$HgCl_2$	...	...	2·5 g.
KI	...	...	8 g.
Water	...	...	100 c. c.

10% Na_2CO_3 solution and Kahlbaum's purest glacial acetic acid (without any iodine value) have been used throught except in the case of furfural where sodium carbonate had been replaced by caustic soda

General Procedure.—Sugar solution was mixed with potassium mercuric iodide solution (25-35 c. c.) in a litre flask and to this Na_2CO_3 solution (50 c. c.) was added. The mixed solution was boiled (8-10 minutes) until grey metallic mercury deposited at the bottom and the supernatant liquid became clear. The flask was then cooled, glacial acetic acid (15 c. c.) added and excess of standard iodine solution (25-50 c. c.) poured in and the contents thoroughly shaken till mercury went completely into the solution. The excess of iodine was then titrated back with standard thiosulphate. The following table gives results with arabinose.

TABLE I.

Arabinose.

Arabinose soln. taken = 5 c.c. 50 C. c. of 0·9979$N/10-I_2$ soln. added. Conc of hypo = 0·9951$N/10$.

Arabinose.	Volume of hypo required Before oxidation. A.	After oxidation. B.	Arabinose found (A—B) × hypo conc. × 0·0075.	Present.
0·6922 g./100 c.c.	50·15 c.c.	45·4 c.c.	0·03545 g.	0·03461 g.
0·6922	50·15	45·5	0·03470	0·03461
0·6262	50·15	46·0	0·03096	0·03131
0·6262	50·15	45·95	0·03134	0·03131
0·3461	25·1	22·8	0·01716	0·017305
0·3461	25·1	22·8	0·01716	0·017305

TABLE II.

Laevulose.

Conc. = 1·5750 g. in 250 c. c. Vol. taken = 10 c. c.
50 C.c. of 1·052$N-I_2$ soln. added.

1·0676 $N/10$-hypo required		Laevulose	
Before oxidation. A.	After oxidation. B.	(A − B) × 1·0676 × 0·0036.	Present.
49·3 c.c.	32·9 c.c.	0·06302 g.	0·063 g.
49·3	32·85	0·06322	0·063
49·3	32·95	0·06284	0·063
49·3	32·9	0·06302	0·063

TABLE III.

Laevulose.

50 C. c. of I_2 soln. added.

			Volume of hypo required				
Laevulose (g./100 c.c.)	Vol.	Conc. of I_2 soln. ($N/10$)	Before oxidation A.	After oxidation B.	Conc. of hypo ($N/10$) C	Found (A − B) × C × 0·0036	Present.
0·8327	5 c.c.	0·6342	32·2 c.c.	20·45c.c.	0·9846	0·04166g.	0·04164g.
0·8327	5	0·6342	32·2	20·5	0·9846	0.04148	0·04164
0·7082	5	0·6342	32·2	22·2	0·9846	0·03545	0·03541
0·7082	5	0·6342	32·2	22·25	0·9846	0·03527	0 03541
0·4593	10	0·9979	50·15	37·55	0·9951	0·04513	0·04593
0·4593	10	0·9979	50·15	37·45	0·9951	0·04548	0·04593

It has been found that best results are obtained within 1-0·5% concentration. The amount of sodium carbonate solution is important, as with lesser quantities than those prescribed low results are obtained.

In the case of cane sugar, it was hydrolysed by hydrochloric acid in the usual way and the acid was then neutralised by sodium carbonate solution. The estimation was then done with this hydrolysed product giving the following results.

TABLE IV.

Cane sugar.

5 C.c. of cane sugar soln. and 50 c. c. of I_2 soln. added.

		Vol. of Hypo required			Cane sugar	
Cane sugar (g./100 c.c.).	Conc of I_2 soln. ($N/10$).	Before oxidation A.	After oxidation B.	Conc. of hypo ($N/10$) C.	Found (A − B) × C × 0·0038.	Present.
0·8082	0·9979	50·15 c.c.	39·45 c.c.	0·9951	0·04046 g.	0·04041 g.
0·8082	0·9979	50·15	39·55	0·9951	0·04007	0·04041
0·7892	1·161	58·7	48·25	0·9897	0·03930	0·03946
0·7892	1·161	58·7	48·3	0·9897	0·03911	0·03946
0·7616	1·169	61·9	51·4	0·9445	0·03769	0·03808
0·7616	1·169	61·9	51·35	0·9445	0·03787	0·03808
0·5044	1·169	61·9	54·9	0·9445	0·02513	0·02522
0·5044	1·169	61·9	54·9	0·9445	0·02513	0·02522

Both lactose and maltose contain one molecule of water of crystallisation which is only expelled by heating at 135-140° for about an hour but during this heating the substance partially carbonises. Hence vacuum heating was restored to as described before. The following tables give the results obtained.

TABLE V.

Lactose.

10 C.c. of lactose solution and 50 c. c. of 0·9972 $N/10$-I_2 soln. added. Conc. of hypo=0·9776$N/10$.

Lactose	Volume of hypo required		Lactose	
	Before oxidation A.	After oxidation B.	(A − B) × strength of hypo × 0·0684.	Present.
0·8166 g./100 c.c.	51 c.c.	39 c.c.	0·08026 g.	0·08166 g.
0·8166	51	39	0·08026	0·08166
0·6848	51	40·85	0·06797	0·06848
0·6848	51	40·8	0·06822	0·06848
0·5226	51	43·2	0·05217	0·05226
0·5226	51	43·3	0·05150	0·05226

TABLE VI.

Maltose.

10 C.c. maltose solution and 50 c.c. of 1·0495 $N/10$-iodine added. Conc. of hypo = 1·015 $N/10$.

Maltose.	Volume of hypo required Before oxidation A.	After oxidation B.	Maltose Found (A − B) × strength of hypo × 0·00684.	Present.
0·84856 g./100 c.c.	51·7 c.c.	39·45 c.c.	0·08504 g.	0·084856 g.
0·84856	51·7	39·5	0·08470	0·084856
0·6348	51·7	42·55	0.06352	0·06348
0·6348	51·7	42·6	0·06317	0·06348
0·4544	51·7	45·15	0·04546	0.04544
0·4544	51·7	45·25	0·04478	0·04544

In the case of furfural Merck's pro-analysi product was taken, dried overnight with anhydrous sodium sulphate and redistilled. The general procedure was the same as that described before with the exception that caustic soda (10%) solution was used instead of sodium carbonate solution.

TABLE VII.

Furfural.

50 C.c. of 1·002 $N/10$-I_2-soln. added and 1·018 $N/10$-hypo used.

Furfural.	Vol.	Volume of hypo required Before oxidation A.	After oxidation B.	Furfural Found (A − B) × strength of hypo × 0·0048.	Present.
1·7484 g/100 c.c.	5 c.c.	49·25 c.c.	31·65 c.c.	0.08596 g.	0·08742 g.
1·7484	5	49·25	31·6	0·08601	0·08742
1·1027	10	49·25	26·75	0·1099	0·11027
1·1027	10	49·25	26·75	0·1099	0·11027
0·8673	10	49·25	31·5	0·0867	0·08673
0·8673	10	49·25	31·6	0·0862	0·08673

This method of estimation of furfural has been found to give good results in presence of acetone (private communication from Dr. H. K. Sen).

Micro-estimation of glucose gave the following results.

TABLE VIII.

Micro-estimation of glucose.

Volume of glucose solution (0·1116 g. in 100 c.c.) used = 0·1 c.c. 1·0126 *N*/100 iodine added = 2 c.c. 1·0126 *N*/100-hypo used.

Volume of hypo required		Glucose found	Glucose present.
Before oxidation A.	After oxidation B.	(A-B) × 1·0126 × 0·00045.	
2 c.c.	1·76 c.c.	0·0001093 g.	0·0001116 g.
2	1·75	0·0001139	0·0001116
2	1·76	0·0001093	0·0001116

In the case of estimation of blood sugar by the micromethod described above, the blood was deprotinised according to the principles of Somogyi's method (*J. Biol. Chem.*, 1930, **86**, 655). Blood (0·1 c.c.) was mixed with a mixture of zinc sulphate (5 c.c. of 0·45%) and KOH solution (1 c.c. of *N*/10). The mixture was heated for 4 minutes by immersing in water-bath and filtered through a small filter. The filter paper was then washed twice with warm water (in 3 c.c. portions). To this 1 c.c. of potassium mercuric iodide solution (previous concentration diluted 10 times) and 2 c.c. of sodium carbonate solution (1%) were added. The mixture was heated in the usual way in a test tube (for 10 minutes), cooled, acidified with pure acetic acid solution (2 c.c. of 3%). 2 C.c. of *N*/100-iodine solution were then added and the test-tube shaken and the excess of iodine was titrated back with dilute thiosulphate solution using micro pipette and micro burette. The following are the results.

TABLE IX.

Blood sugar.

Vol. of blood taken = 0·1 c.c. Vol. of Iodine solution added = 1 c.c.

Conc. of I_2	Volume of hypo required		Conc. of hypo.	Sugar in blood (A-B) × strength × 0·225.
	Before oxidation A.	After oxidation B.		
1·0126 *N*/100	2 c.c.	1·4 c.c.	1·0126 *N*/200	0·1367 %
1·0126 *N*/100	2	1·4	1·0126 *N*/200	0·1367
1·9998 *N*/200	1·98	1·38	1·01 *N*/200	0·1363
1·9998 *N*/200	1·98	1·395	1·01 *N*/200	0·1329
1·8959 *N*/200	1·83	1·39	1·036 *N*/200	0·1026
1·8959 *N*/200	1·83	1·39	1·036 *N*/200	0·1026

Hagendorn and Jenson's potassium ferricyanide method of estimation of blood sugar gave the following results with the same samples of blood.

TABLE X.

Blood sugar.

Vol. of blood taken = 0·1 c.c. Vol. of 0·1802% potassium ferricyanide added = 2 c.c.

Volume of hypo required		Conc. of Hypo	Sugar in blood (A-B) × strength × 0·177*
Control tube.	With blood sugar.		
1·745 c.c.	1·155 c.c.	1·0126 *N*/200	0·1057%
1·745	1·155	1·0126 *N*/200	0·1057
1·75	1·17	1·01 *N*/200	0·1037
1·75	1·18	1·01 *N*/200	0·1019
1·65	1·25	1·036 *N*/200	0·07336
1·65	1·25	1·036 *N*/200	0·07336

In conclusion we wish to express our sincere thanks and gratitude to Mr. P. B. Sen for his kind assistance in the estimation of blood sugar and to Prof. Dr. H. K. Sen, for the interest which he has taken and the occasional help and advice he has so kindly given throughout the progress of the work.

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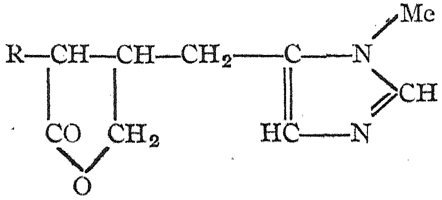
Syntheses in Furan Series. Part I. Synthesis of 2-Ketotetrahydrofuran-4-acetic Acid.

BY RANAJIT GHOSH.

The present investigation was undertaken with a view to synthesise complex furan bodies related to the furan skeleton present in the glyoxaline alkaloids of *Pilocarpus Jaborandi* (Jowett, *J. Chem. Soc.*, 1900, **77**, 474, 851 ; 1901, **79**, 581, 1331 ; 1903, **83**, 442 ; 1905, **87**, 794 ; *cf.* Pinner, *Ber.*, 1900, **33**, 1428, 2537 ; 1901 **34**, 727 ; 1902, **35**, 204, 2443 ; 1905, **38**, 1510 ; Pyman, *J. Chem. Soc.*, 1910, **97**, 1814) and of *Pilocarpus Microphyllus* (Pyman, *Proc, Chem. Soc.*, 1912, 267 ; *J. Chem. Soc.*, 1912, **101**, 2260). Syntheses of pilopic acids by Tschitschibabin (*Ber.*, 1930, **63**, 460) and by Welch (*J. Chem. Soc.*, 1931, 1370) and of homopilopic acids by Preobrashenski and others (*Ber.*, 1934, **67**, 710 ; 1935, **68**, 850), have lent more support to the constitution attributed to the furan portion of the alkaloids, pilocarpine, *iso*pilocarpine etc. by Jowett (*loc. cit.*). Moreover, the alkaloids themselves have been synthesised from the above acids (Preobrashenski and others, *Ber.*, 1933, **66**, 536, 1187). The alkaloid pilosine from *Pilocarpus microphyllus* to which Pyman (*loc. cit.*) has given a structure similar to that of pilocarpine (Jowett, *loc. cit.*) may be observed to contain almost the same furan skeleton as pilocarpine etc., with the difference that the former contains one $C_6H_5 \cdot CHOH$-group in place of C_2H_5-group in the latter. Pilosinine obtained from pilosine by treatment with caustic potash has been described by Pyman (*loc. cit.*) as pilocarpine without its ethyl group. The relation existing among these bodies is as follows :



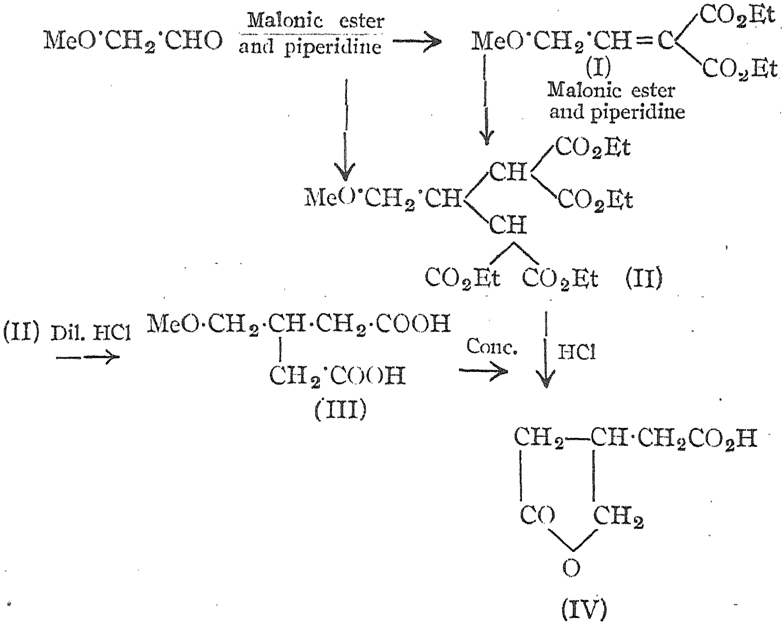
where R=Et in pilocarpine, Ph·CHOH in pilosine and H in pilosinine ; pilocarpidine having $R=C_2H_5$ and NH for N·Me (*cf.* Jowett, *loc. cit.*).

Although the above structures for pilosine and pilosinine have been mainly based on some physiological and a few chemical properties, (*cf.* Pyman, *loc. cit.*) no attempts, as yet, have been made to settle the constitution of the alkaloids by synthesis. Syntheses of the formulated skeletons being necessary to come to a definite conclusion regarding their constitutions, the present investigation was undertaken to synthesise furan bodies from which the more complex system of the alkaloids could be built up.

The furan acid, 2-ketotetrahydrofuran-4-acetic acid, which is the parent compound of such lactonic acids and which is also present in pilosinine skeleton, has been described in the present paper. The methods adopted by the previous workers, Preobrashenski and others (*loc. cit.*), have been based on the synthesis of a higher homologous acid from a lower homologous one but the present synthesis has been achieved by the following simple manner, the method being of sufficiently general applicability.

These lactonic acids, 2-ketotetrahydro-furan-4-acetic acid and its derivatives, are isomeric with paraconic acids, and they are glutaric acids with two substituents, one in the α-position and the other in the β-position. The substituent in the α-position is an alkyl group (*cf.* Jowett, Pyman, *loc. cit.*), whereas the substituent in the β-position is always an oxymethyl group ($-CH_2 \cdot OH$), the hydroxyl group of which helps in the formation of the lactone ring. This necessitates the synthesis of these lactonic bodies from hydroxy-acetaldehyde and malonic ester following the well known synthesis of glutaric acid, the substituent in the α-position being subsequently introduced into the alkylidene dimalonic ester by the usual methods.

Methoxyacetaldehyde has been condensed with malonic ester in presence of piperidine yielding methoxyethylidene monomalonic ester (I) and methoxyethylidene dimalonic ester (II). The dimalonic ester, also obtainable from (I) by further treatment with malonic ester and piperidine, has been hydrolysed to β-methoxymethylglutaric acid (III) which ultimately on demethylation yields 2-ketotetrahydro-furan-4-acetic acid (IV) according to the following scheme.


MeO·CH2·CHO
Malonic ester and piperidine
MeO·CH2·CH=C(CO2Et)2
(I)
Malonic ester and piperidine
MeO·CH2·CH<CH(CO2Et)2, CH(CO2Et)2
(II)
(II) Dil. HCl
MeO·CH2·CH(CH2·COOH)·CH2·COOH
(III)
Conc. HCl
CH2—CH·CH2CO2H, CO, CH2, O
(IV)

The hydrolysis and ring-closure can be effected in one step by heating (II) with fuming hydrochloric acid in a sealed tube at 160-180°. The methoxyacetaldehyde, previously obtained in very small quantities (*J. Biol. Chem.*, 1934, **104**, 511), has now been obtained in better yield by modifying the oxidation of the glycol-ether (*vide* experimental). A fairly concentrated solution of methoxyacetaldehyde was obtained contaminated with traces of ethyleneglycol monomethyl ether, the presence of which was neglected considering the fact that in no way it interfered with the condensation of the aldehyde with malonic ester under the experimental conditions.

The lactonic nature of the acid was proved by titration. In the cold, it was titrated directly with *N*/10-baryta (and also with *N*/10-NaOH) when the equivalent weight (144·4) agreed with the calculated value (144·0, if one COOH is present). Boiled with excess of *N*/10-sodium hydroxide and the excess of alkali titrated back with *N*/10-sulphuric acid, the equivalent weight turned out to be 71·34 for 72, calculated on the basis that the acid (IV) contains one COOH group and one lactonic group.

Substituting one of the reactive hydrogen atoms of methoxyethylidene dimalonic ester with C_2H_5-group it has been possible to synthesise homopilopic acids (to be communicated shortly). The replacement of one of the reactive hydrogen atoms of the same ester by $C_6H_5{\cdot}CH_2$ is in progress and this along with condensation of γ-methoxycrotonic ester (and also γ-ethoxy crotonic ester) with malonic and cyanoacetic esters will form the subject matter of a future communication.

EXPERIMENTAL.

Methoxyacetaldehyde.—Ethyleneglycol monomethyl ether (90 c.c.), dissolved in water (40 c.c.) was heated to boiling in a two necked 1000 c.c. round bottomed flask fitted with a dropping funnel and a fractionating column joined to a long condenser containing ice-water. A solution of pure sodium dichromate (132 g.) in water (160 c.c.) was mixed with concentrated sulphuric acid (*d* 1·84, 96 c.c.) and the mixture allowed to drop into the flask from the dropping funnel. The dropping of the liquid in the funnel was so regulated that the rate of addition was almost the same as the rate of distillation. The reaction was complete in about 45 minutes. The distillate coming at 99−101° was collected in a flask placed in a freezing mixture bath. About 180 c.c. of methoxyacetyldehyde solution were obtained.

Ethyl Methoxyethylidene Monomalonate.—To the methoxyacetaldehyde solution (180 c.c.) ethyl malonate (100 c.c.) was added and after cooling the mixture in ice, piperidine (8−9 c.c.) was dropped into it. The mixture was kept in ice for 24 hours after which it was reheated on the water-bath for 7 hours. The liquid was then cooled, extracted with ether, washed successively with dilute hydrochloric acid, soda solution and water, dried over calcium chloride and finally distilled after removal of ether. The distillate was collected in three fractions: the first fraction containing mainly malonic ester, the second fraction (b.p. 120-140°/8 mm.) was repeatedly fractionated and collected at 128-130°/8 mm. [Found: C, 55·38; H, 7·50; M.W. (cryoscopic in benzene) 217, 218. $C_{10}H_{16}O_5$ requires C, 55·55; H, 7·40 per cent. M.W., 216]. That the liquid is unsaturated is proved by the fact that it decolourises bromine both in organic solvents and in water.

Ethyl Methoxyethylidene Dimalonate (1st method).—The third fraction obtained in the previous experiment was repeatedly fractionated and a slightly thick liquid was collected at 190-200°/10 mm. [Found: C, 54·12; H, 7·42. M.W. (cryoscopic), 373. $C_{17}H_{28}O_9$ requires C, 54·25; H, 7·44 per cent. M.W., 376].

Ethyl Methoxyethylidene Dimalonate (2nd method).—Ethyl methoxyethylidene monomalonate (20 g.) was mixed with excess of malonic ester (30 g.) and piperidine (0·5 g.) and the mixture was heated on the water-bath for 6 hours. The liquid was then taken in ether and washed successively with dilute hydrochloric acid, soda solution and finally with water. The ether solution was then dried over calcium chloride and finally distilled at 190-200°/10 mm. [Found: C, 53·86; H, 7·65; M.W. (cryoscopic in benzene), 375. $C_{17}H_{28}O_9$ requires C, 54·25; H, 7·44 per cent. M.W., 376).

In an experiment, glycol monomethyl ether (25 g.), malonic ester (105 g.) and a little piperidine (2·5 g.) were heated for 8 hours on the water-bath as in the above experiments. The materials, isolated in the usual way, were distilled and the liquids separated almost quantitatively into malonic ester and ethyleneglycol monomethylether without a trace of any higher boiling substance. This shows that ethyleneglycol monomethylether does not interfere with the condensation of the aldehyde with malonic ester.

β-Methoxymethylglutaric Acid.—A mixture of ethyl methoxyethylidene dimalonate (25 g.) and hydrochloric acid (*d* 1·19, 50 c.c.) and water (50 c.c) was boiled under reflux for 6 hours during which the oil gradually disappeared. The liquid was in one experiment evaporated to dryness and distilled in vacuum and in another the acid solution was neutralised with sodium carbonate and extracted with ether. The alkaline aqueous solution was then acidified and repeatedly extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and distilled. The distillate in both the experiments came over at 184-190°/4 mm. (Found: C, 47·5; H, 6·85; Equiv., 90. $C_7H_{12}O_5$ requires C, 47·7; H, 6·8 per cent. Equiv., 88).

β-Methoxymethylglutaric Anhydride.—The glutaric acid (5 g.) from the previous experiment was mixed with acetic anhydride (15 c.c.) and heated under reflux on a sand-bath for 3 hours. The acetic anhydride was then removed on the water pump and the anhydride distilled at 145-152°/7 mm. It solidified at once and melted at 77-78°. (Found: C, 53·05; H, 6·5. $C_7H_{10}O_4$ requires C, 53·16; H, 6·3 per cent).

Ethyl β-Methoxymethylglutarate.—Methoxymethylglutaric acid (17·6 g.) was added to an alcoholic solution of sodium ethoxide (1·6 g. of Na in 200 c.c. of absolute alcohol) and refluxed for 9 hours with excess of ethyl bromide (55 g.). Alcohol and ethyl bromide were then distilled off as far as possible and the residual mass was then cooled, treated with water and extracted with ether in the usual way.

A liquid was collected at 125-135°/8 mm. [Found: C, 57·06; H, 8·58; M.W. (cryoscopic in benzene), 228. $C_{11}H_{20}O_5$ requires C, 56·90; H, 8·62 per cent. M.W., 232).

2-Ketotetrahydrofuran-4-acetic Acid.— β-Methoxymethylglutaric acid (3 g.) was heated at 160-180° for 3 hours in a sealed tube with hydrochloric acid (12 c.c., *d* 1·19). It was then cooled and the product filtered and distilled in vacuum after removal of water at the water pump. A viscous liquid, which solidified on cooling, was obtained at 200-208°/10 mm. It was repeatedly crystallised from a mixture of chloroform and ether when it melted at 87-88°. It is soluble in water, alcohol, chloroform, benzene, etc. It is not much soluble in ether, from which it can also be crystallised. (Found: C, 49·89; H, 5·31. $C_6H_8O_4$ requires C, 49·99; H, 5·55 per cent). Directly titrated in the cold with *N*/10-baryta and also with *N*/10 caustic soda it gave equiv. 144·4. $C_6H_8O_4$ requires (for one COOH- group) equiv., 144·0. When the acid was boiled with excess of NaOH for ½ hour, cooled and the excess of alkali titrated with *N*/10-H_2SO_4, the equiv. wt. was 71·34. $C_6H_8O_4$ requires for one lactone group and one COOH group the equiv. wt. 72.

Ethyl methoxyethylidene dimalonate (5 g.) was heated to 180° for 5 hours in a sealed tube with concentrated HCl (*d* 1·19, 15 c.c.). The product when cold was neutralised with $NaHCO_3$ and extracted with ether. The solution of the sodium salt in water was then acidified with hydrochloric acid and repeatedly extracted with ether. The ethereal layer, dried over anhydrous sodium sulphate, gave on evaporation a thick oil which solidified on keeping. It was purified from ether-chloroform mixture, m.p. 87-88°; b.p. 200-208°/10 mm. (Found: C, 49·75; H, 5·64. $C_6H_8O_4$ requires C, 49·99, H, 5·5 per cent). Found: equiv., 143·3 with *N*/10-NaOH in the cold. Boiled with excess *N*/10-NaOH, equiv. was found to be 72·2. A mixed melting point of this with a sample obtained by the first method was determined and it was also 87-88°.

In conclusion I wish to express my sincere thanks to Sir P. C. Rây for the kind interest he took during the investigation and also for placing the resources of his laboratory at my disposal.

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A Critical Examination of Pascal's Value for the Magnetic Susceptibility of the CH_2-group.

By S. S. Bhatnagar and N. G. Mitra.

In a previous paper (*Phil. Mag.*, 1934, **18**, 449) we had a critical examination of the susceptibilities of several homologous series and we found that the value for the CH_2-group is of the order of $-11{\cdot}36 \times 10^{-6}$ as against Pascal's value of $-12{\cdot}35 \times 10^{-6}$, which when corrected for the new value for water comes out at $-11{\cdot}86$. It was shown that the lower value for the CH_2-group yields a value of χ_H of the order $-2{\cdot}68 \times 10^{-6}$ as against $-2{\cdot}98 \times 10^{-6}$ which is the figure obtained from Pascal's value of the CH_2-group. The theoretical value for χ_H is $-2{\cdot}37 \times 10^{-6}$ and is in fair agreement with our value.

We have now critically examined Pascal's data and find that Pascal adopted the mean $-12{\cdot}35 \times 10^{-6}$ by a study of twenty four compounds comprising seven different series. Pascal later carried out numerous investigations extending to over 80 substances in different series. As the accuracy of his later work has been generally recognised, we have included all his data in our list for a re-examination of his values.

The atomic weights employed by Pascal were slightly different from the modern atomic weights adopted by us. As the molecular susceptibilities are obtained by multiplying molecular weights with specific susceptibilities, we find that the employment of newer values of the molecular weights causes an appreciable change in the calculated value of χ for the CH_2-group. This procedure is justified irrespective of the accuracy of susceptibility measurements as Pascal would have done the same thing if the values now known to be established were accepted in his time.

The specific susceptibility of carbon as measured by Pascal with great precision from his experiments on carbon, prepared from recrystallised white sugar, was $-5{\cdot}2 \times 10^{-6}$. The atomic susceptibility for carbon as given by him was $-6{\cdot}25 \times 10^{-6}$. From this, we find the atomic weight of carbon, as taken by Pascal, was

$$\frac{-6{\cdot}25 \times 10^{-6}}{-5{\cdot}2 \times 10^{-6}} = 12{\cdot}02,$$

instead of 12·00 which is the value adopted at present The values for hydrogen and nitrogen were 1·008 and 14·01 against 1·0077 and 14·008 now given in the International Critical Tables. In our previous paper, as also in this one, the molecular weights of the compounds were calculated by using atomic weights now accepted as given in the International Critical Tables, 1923 Ed.

In the tables given below we have gathered together the susceptibilities of nearly all the compounds useful for these determinations and examined by Pascal in his monumental work.

TABLE I.

Hydrocarbons.

	$\chi_M \times 10^{-6}$.	Pascal's value $\chi_{CH_2} \times 10^{-6}$.	Corrected value $\chi_{CH_2} \times 10^{-6}$.
	Aliphatic.		
Hexane, C_6H_{14}	$-79·6$		
		$-12·05$	$-12·02$
Octane, C_8H_{18}	$-103·7$		
		$-13·00$	$-12·99$
Decane, $C_{20}H_{22}$	$-129·7$		
	Aromatic.		
Benzene, C_6H_6	$-57·4$		
		$-12·50$	$-12·49$
Toluene, C_7H_8	$-69·9$		
		$-12·20$	$-12·18$
1 :3-Xylene, C_8H_{10}	$-82·1$		
Diphenyl, $C_{12}H_{10}$	$-108·7$		
		$-11·30$	$-11·27$
Diphenylmethane, $C_{13}H_{12}$	$-120·0$		
	Unsaturated.		
*Styrolene, C_8H_8	$-71·0$		
		$-12·40$	$-12·38$
*α-Methylstyrolene, C_9H_{10}	$-83·4$		
		$-11·10$	$-11·07$
*αβ-Dimethylstyrolene, $C_{10}H_{12}$	$-94·5$		
Trimethylethylene, C_5H_{10}	$-56·4$		
		$-12·26$	$-12·23$
Octylene, C_8H_{16}	$-93·2$		
Diallyl, C_6H_{10}	$-57·4$		
		$-12·25$	$-12·20$
Dimethyl-2 :4-hexadiene, C_8H_{14}	$-81·9$		

* These names have been changed in the present nomenclature as : Styrene, α-methylstyrene and αω—dimethylstyrene.

TABLE II.

Oxygenated compounds.

	$\chi_M \times 10^{-6}$.	Pascal's value $\chi_{CH_2} \times 10^{-6}$.	Corrected value $\chi_{CH_2} \times 10^{-6}$.
		Alcohols.	
Ethyl alcohol, C_2H_6O	−35·7		
		−12·20	−12·17
Propyl alcohol, C_3H_8O	−47·9		
		−12·26	−12·25
Octyl alcohol, $C_8H_{18}O$	−109·2		
*iso*Butyl alcohol, $C_4H_{10}O$	−61·6		
		−11·70	−11·67
*iso*Amyl alcohol, $C_5H_{12}O$	−73·3		
*tert*Butyl alcohol, $C_4H_{10}O$	−61·7		
		−12·10	−12·08
*tert*Amyl alcohol, $C_5H_{12}O$	−73·8		
		Acids.	
Formic acid, CH_2O_2	−20·70		
		−12·20	−12·18
Acetic acid, $C_2H_4O_2$	−32·90		
		−12·40	−12·37
Propionic acid, $C_3H_6O_2$	−45·30		
		−12·70	−12·70
Butyric acid, $C_4H_8O_2$	−58·00		
*iso*Butyric acid, $C_4H_8O_2$	−59·20		
		−11·30	−11·28
*iso*Valeric acid, $C_8H_{10}O_2$	−70·50		
		Aldehydes.	
Acetaldehyde, C_2H_4O	−23·00		
		−12·40	−12·37
Propionaldehyde, C_3H_6O	−35·40		
		−12·30	−12·28
Butyraldehyde, C_4H_8O	−47·70		
		−12·20	−12·19
* Amylaldehyde, $C_5H_{10}O$	−59·90		
		−12·50	−12·48
Enanthylaldehyde, $C_7H_{14}O$	−84·90		
		Ketones.	
Acetone, C_3H_{10}	−35·1		
		−12·40	−12·35
Methylethyl ketone, C_4H_8O	−47·5		
		−12·40	−12·40
Methylpropyl ketone, $C_5H_{10}O$	−59·9		
		−12·10	−12·04
Methylbutyl ketone, $C_6H_{12}O$	−72·0		
		−12·60	−12·56
Methylhexyl ketone, $C_8H_{16}O$	−97·2		
		Esters.	
Methyl acetate, $C_3H_6O_2$	−45·5		
		−12·00	−11·95
Ethyl acetate, $C_4H_8O_2$	−57·5		
Methyl bromoacetate, $C_3H_5O_2Br$	−74·1		
		−12·30	−12·29
Ethyl bromoacetate, $C_4H_7O_2Br$	−86·4		
Methyl acetate, $C_3H_6O_2$	−45·5		
		−12·10	−12·04
Methyl propionate, $C_4H_8O_2$	−57·6		

* Present nomenclature : *iso*Valeraldehyde.

TABLE III.

Halogenated compounds.

	$\chi_M \times 10^{-6}$.	Pascal's value $\chi_{CH_2} \times 10^{-6}$.	Corrected value $\chi_{CH_2} \times 10^{-6}$.
Propyl chloride, C_3H_7Cl	−58·1		
		−12·32	−12·28
Octyl chloride, $C_8H_{17}Cl$	−119·7		
Ethyl bromide, C_2H_5Br	−55·5		
		−12·00	−11·93
Propyl bromide, C_3H_7Br	−67·5		
*iso*Propyl bromide, C_3H_7Br	−67·8		
		−12·30	−12·25
*iso*Amyl bromide, $C_5H_{11}Br$	−92·4		
Acetyl chloride, C_2H_3OCl	−40·3		
		−12·20	−12·19
Butyryl chloride, C_4H_7OCl	−64·7		
Ethylene chloride, $C_2H_4Cl_2$	−62·1		
		−12·33	−12·31
Amylene chloride, $C_5H_{10}Cl_2$	−99·1		
Ethylene bromide, $C_2H_4Br_2$	−82·5		
		−12·30	−12·28
Amylene bromide, $C_5H_{10}Br_2$	−119·4		
		−12·43	−12·35
Octylene bromide, $C_8H_{16}Br_2$	−156·7		

TABLE IV.

Nitrogenous compounds.

	$\chi_M \times 10^{-6}$.	Pascal's value $\chi_{CH_2} \times 10^{-6}$.	Corrected value $\chi_{CH_2} \times 10^{-6}$.
Methylamine, CH_5N	−28·1		
		−11·80	−11·77
Diethylamine, $C_4H_{11}N$	−63·5		
*iso*Butylamine, $C_4H_{11}N$	−64·2		
		−12·48	−12·45
Di-*iso*butylamine, $C_8H_{19}N$	−114·1		
		−12·30	−12·26
Tri-*iso*butylamine, $C_{12}H_{27}N$	−163·3		
*iso*Amylamine, $C_5H_{13}N$	−77·0		
		−12·32	−12·30
Di-*iso*amylamine, $C_{10}H_{23}N$	−138·6		
		−12·30	−12·27
Tri-*iso*amylamine, $C_{15}H_{33}N$	−200·1		
Aniline, C_6H_7N	−65·1		
		−12·40	−12·38
Methylaniline, C_7H_9N	−77·5		
		−12·00	−11·97
Ethylaniline, $C_8H_{11}N$	−89·5		
Methylaniline, C_7H_9N	−77·5		
		−12·20	−12·09
Dimethylaniline, $C_8H_{11}N$	−89·7		
Azobenzene, $C_{12}H_{10}N_2$	−116·0		
		−12·35	−12·27
Azotoluene, $C_{14}H_{14}N_2$	−140·7		
Amidoazobenzene, $C_{12}H_{11}N_3$	−123·3		
		−12·40	−12·38
Amidoazotoluene, $C_{14}H_{15}N_3$	−148·1		
Nitrobenzene, $C_6H_5NO_2$	−64·1		
		−11·90	−11·88
1 : 2-Nitrotoluene, $C_7H_7NO_2$	−76·0		

TABLE V.

Acetylenic compounds.

		$\chi_{M} \times 10^{-6}$.	Pascal's value $\chi_{CH_2} \times 10^{-6}$.	Corrected value. $\chi_{CH_2} \times 10^{-6}$.
Acetyl phenylacetylene,	$C_{10}H_8O$	−86·9		
			−12·10	−12·08
Propionyl ,,	$C_{11}H_{10}O$	−99·0		
			−11·90	−11·88
Butyryl ,,	$C_{12}H_{12}O$	−110·9		
			−13·00	−12·98
Valeryl ,,	$C_{13}H_{14}O$	−123·9		
			−11·70	−11·68
Caproyl ,,	$C_{14}H_{16}O$	−135·6		

In Tables I—V, column 3 gives the value of CH_2- group calculated according to Pascal's atomic weights. In column 4 are given the values for the same group, when calculated with the aid of the now accepted atomic weights. The mean of all the values of column 3 yields a figure of −12·20 instead of −12·35 as given by Pascal for the first 24 substances examined by him. In column 4 the newer atomic weights reduce this to $-12{\cdot}17 \times 10^{-6}$ which when corrected for water would yield a figure of −11·68.

From Perkin's observations on magneto-optical rotation and the data on viscosities and surface tension in relation to chemical constitution, it has been shown that in comparing physical properties for investigating chemical constitution, the first member of the homologous series generally leads to erroneous results. If we employ a similar procedure and reject the values for the first member in a series, the value for CH_2 comes even less than −11·68 and assumes a magnitude somewhat nearer to our value.

Recently Gray and Cruikshank (*Trans. Faraday Soc.*, 1935, **31**, 1421) mentioned to have obtained a value of −11·87 for a single CH_2-group from an investigation on three different homologous series of organic nitrites, nitrates and nitro compounds. The organic nitrites and nitrates were not investigated by us as they are difficult to obtain in a pure state, specially the aliphatic nitrites, on account of their tendency to decompose, particularly in glass vessels. Moreover, it is by no means certain that the organic nitrites do not show the tautomerism characteristic of HNO_2 metal derivatives. For example, it has not been definitely proved that a sample of methyl nitrate has no nitromethane in equilibrium with it. Pascal in his numerous investigations on the susceptibilities of organic compounds has not included many of the nitro compounds and still less the nitrates and the nitrites. The only nitro bodies investigated by him were nitrobenzene and nitrotoluene and the difference in this case for a CH_2-group is $-11{\cdot}90 \times 10^{-6}$ which when corrected for the new value of water, is reduced to $-11{\cdot}42 \times 10^{-6}$, a figure quite in proximity with our value of $-11{\cdot}36 \times 10^{-6}$.

Further work on the subject is in progress.

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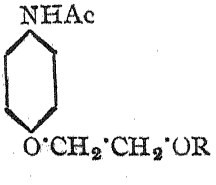
Preparation of Compounds Related to Phenacetin.

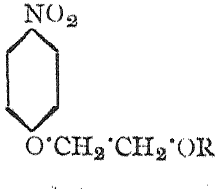
BY (MISS) B. N. KATRAK.

This work was undertaken with a view to prepare substances related to phenacetin (I) particularly those containing an acetyl group in the ethoxy side-chain. The following were prepared:—

(1) β-Hydroxy-*p*-nitrophenetole (II, R=H). (2) β-Acetoxy-*p*-nitrophenetole (II, R=Ac). (3) β-Benzoyloxy-*p*-nitrophenetole (II, R=Bz). (4) β-Salicyloxy-*p*-nitrophenetole (II, R=Salicyl). (5) β-Chloro-*p*-nitrophenetole (II, where Cl takes the place of OR in the side-chain). (6) β-Hydroxy-*p*-acetylaminophenetole (I, R=H). (7) β-Acetoxy-*p*-acetylaminophenetole (I, R=Ac). (8) β-Hydroxy-*o*-nitrophenetole (9) β-Acetoxy-*o*-nitrophenetole. (10) β-Benzoyloxy-*o*-nitrophenetole. (11) β-Hydroxy-*m*-nitrophenetole.



(I)



(II)

The compounds (6) and (7) were tested at the Haffkine Institute by courtesy of Father Caius S. J., but were found to have no antipyretic action. Preliminary attempts to reduce the nitro compounds to amino compounds were unsuccessful. The compounds prepared are now described as there is no immediate possibility of continuing this work.

EXPERIMENTAL.

*β-Hydroxy-*p*-nitrophenetole.*—Sodium nitrophenate (120 g.), ethylene chlorhydrin (60 g.) and 50% alcohol (150 c. c.) were heated at 120° for 23 hours. The upper oily layer was treated with ether which separated the required product (29 g.) in nearly pure form; a further yield (20 g.) was obtained from the ether extract. The water layer, on concentration, gave a small yield (8 g.). The product is soluble in almost all organic solvents and also moderately in water. It crystallises from benzene in long transparent needles, m. p. 101-2°. (Found : N, 8·1. $C_8H_9O_4N$ requires N, 7·6 per cent).

With acetyl chloride-pyridine the above product gave *β-acetoxy-*p*-nitrophenetole* which crystallises from carbon tetrachloride in transparent rectangular plates, m. p. 85-87°. (Found : N, 6·4. $C_{10}H_{11}O_5N$ requires N, 6·2 per cent).

*β-Benzoyloxy-*p*-nitrophenetole* crystallises from dilute methyl alcohol in clusters of thin transparent plates, m. p. 116°. (Found : N, 5·2. $C_{15}H_{13}O_5N$ requires N, 4·9 per cent).

*β-Salicyloxy-*p*-nitrophenetole.*—β-Hydroxy-*p*-nitrophenetole and salicyl chloride in molecular proportions were kept in a desiccator for 2 days and the resulting mixture was heated at 100° under reduced pressure (water pump) for some hours to remove salicyl chloride. The mixture was extracted with benzene and the residue after evaporation of benzene, was crystallised from carbon tetrachloride, m. p. 133°. (Found : N, 4·67. $C_{15}H_{13}O_6N$ requires N, 4·62 per cent).

*β-Chloro-*p*-nitrophenetole.* —β-Hydroxy-*p*-nitrophenetole was heated with phosphorus pentachloride (1 mol.) at 100° until evolution of hydrogen chloride ceased. The product was mixed with powdered ice, the solid separating, crystallised from benzene-petroleum ether in long, thin needles, m. p. 67-68°. (Found: N 7·3. $C_8H_8O_3NCl$ requires N, 7·0 per cent).

β-Hydroxy-p-*acetylaminophenetole*.—*p*-Acetylaminophenol (27g.), ethylene chlorohydrin (15 g.) and 2*N*-NaOH solution (7·5 g.) were heated at 60-70° for 8 hours, the oil separating (27 g.) solidified when kept at 0°. It crystallised from acetone-benzene in transparent plates, m. p. 116-17°. (Found: N, 7·6. $C_{10}H_{13}O_3N$ requires N, 7·2 per cent). With acetic anhydride-H_2SO_4 it gave *β-acetoxy*-p-*acetylaminophenetole* which crystallised from benzene in shining plates, m. p. 130°. (Found: N, 6·3. $C_{12}H_{15}O_4N$ requires N, 5·9 per cent).

β-Hydroxy-o-*nitrophenetole*.—A mixture of sodium-*o*-nitrophenate (30 g.), ethylene chlorhydrin (15 g.), and water (10 c. c.) was heated at 125° for 20 hours and extracted with ether. The extract was washed with caustic soda solution and water and after drying it was distilled under reduced pressure, b. p. 180°-182°/4 mm., yield 44 g. (Found: N, 7·4. $C_8H_9O_4N$ requires N, 7·6 per cent). The compound gives *β-acetoxy*-o-*nitrophenetole* with acetyl chloride-pyridine, b. p. 201°-202°/4 mm. (Found: N, 6·4. $C_{10}H_{11}O_5N$ requires N, 6·2 per cent).

β-Benzoyloxy-o-*nitrophenetole* crystallises from dilute acetic acid in clusters of transparent plates, m. p. 75-76°. (Found: N, 4·8. $C_{15}H_{13}O_5N$ requires N, 4·9 per cent).

β-Hydroxy-m-*nitrophenetole*.—A mixture of *m*-nitrophenol (2·5 g.) in 40% KOH solution (1 g.) and ethylene chlorhydrin was heated at 100° for 2 hours. The product crystallised from acetone-petroleum ether, m. p. 90-91°, yield 2 g. (Found: N, 7·8. $C_8H_9O_4N$ requires N, 7·6 per cent).

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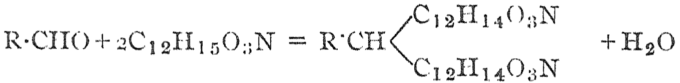
Studies in the Cotarnine Series. Part VII. Action of Sulphuric Acid on Cotarnine: Formation of Methylene-*bis*phenol-betaine of 2-Methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro*iso*quinolinium Hydroxide.

By B. B. Dey and T. K. Srinivasan.

The investigation of the reactivity of the *ana*-hydrogen atom in the narcotine bases has revealed a curious difference between narcotine and hydrocotarnine on the one hand and cotarnine on the other. The former react smoothly with aldehydes in the presence of sulphuric acid to give crystalline dimolecular compounds of the following type:



$$R{\cdot}CHO + 2C_{12}H_{15}O_3N = R{\cdot}CH\begin{cases} C_{12}H_{14}O_3N \\ C_{12}H_{14}O_3N \end{cases} + H_2O$$

(where R = H, Me, etc.)

Cotarnine, however, behaves very differently and remains either unchanged or yields only small amounts of impure amorphous products. This was particularly noticeable in the case of the condensation with formaldehyde which led with hydrocotarnine to the formation of the theoretical quantity of methylene dihydrocotarnine in the course of twelve hours, whereas under identical conditions, no new product could be isolated with cotarnine. This departure from the normal course led to attempts to bring about the reaction by varying the conditions and eventually to a careful study of the action of sulphuric acid alone on cotarnine.

The action of sulphuric acid on the opium alkaloids has been studied by many investigators.[*]

By treatment with 82% sulphuric acid or 73% sulphuric acid at 80° Bandow (*Ber.*, 1897, **30**, 1747) obtained from hydrocotarnine a new base which he named hydrodicotarnine and assigned to it the formula $C_{24}H_{28}O_6N_2$, the reaction was represented thus :—

$$C_{12}H_{15}O_3N + O = H_2O + C_{24}H_{28}O_6N_2.$$

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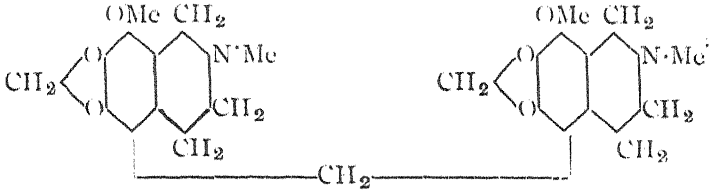
[*] Arpe, *Annalen*, 1845, **55**, 96; Laurent and Gerhardt, *Ann. chim. phys.*, 1848, *iii*, **24**, 112; Mathiessen and Wright, *Ann. Suppl.*, 1870, **7**, 170; Armstrong, *J. Chem. Soc.*, 1871, **24**, 56; Fulton, *J. Lab. Clin. Med.*, 1928, **13**, 750; Kitasato and Goto, *Ber.*, 1930, **63**, 2696.

Freund and Daube (*Ber.*, 1912, **45**, 1183), who repeated this work, showed conclusively that the product isolated was identical with methylene dihydrocotarnine (I), a substance prepared subsequently in theoretical yield from the condensation of hydrocotarnine and formaldehyde under the influence of sulphuric acid. They explained the formation of this base by assuming that the first effect of sulphuric acid on hydrocotarnine in Bandow's experiment was to demethylenate the base, formaldehyde and a phenolic body (2-methyl- 6 : 7- dihydroxy- 8-methoxy-1:2:3:4- tetrahydro*iso*quinoline) being formed : The formaldehyde, split off in the reaction, then condensed with unchanged hydrocotarnine in the presence of sulphuric acid to form methylene dihydrocotarnine (I),

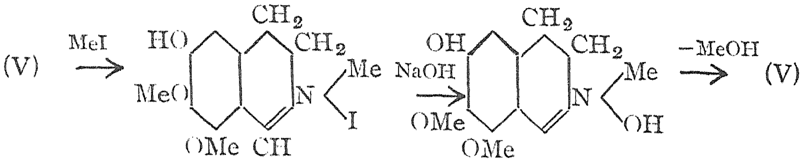


(I)

In the present investigation it is found that the reaction takes a different course when cotarnine is treated with sulphuric acid under conditions very similar to those of Bandow. After standing for three days at room temperature, the acid solution, which acquired a scarlet-red colour, threw down, on basification, a considerable amount of a beautiful orange-yellow substance, m. p. 302-304° (decomp.).

It is necessary to mention here that the duration of the experiment, the concentration of the acid employed and the quantity of the acid are important factors in getting the desired result.

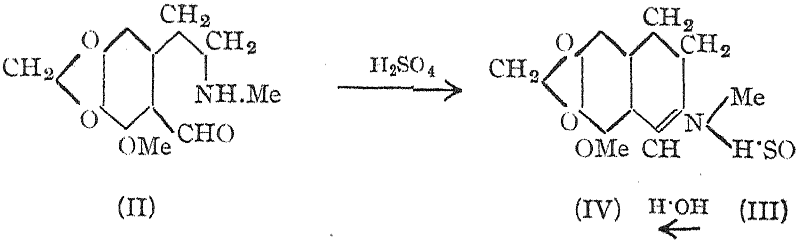
The compound is a fairly strong base and dissolves readily in dilute mineral acids. The dihydrochloride and the dihydrobromide of the base have been obtained in a crystalline condition while with nitric acid it has been possible to prepare both the mono- and the dinitrate. As a phenolic base it dissolves in cold dilute caustic soda to a deep red solution from which it is reprecipitated on treatment with carbon dioxide, and with ferric chloride it gives a dark green colour. The phenolic character of the base is further demonstrated by the easy formation of a methyl ether insoluble in alkalis. Acetylation and benzoylation, however, have not been successful only impure products being obtained. The completely demethylated base and its hydroiodide have also been obtained by the action of hydriodic acid under pressure. The quaternary ammonium iodide of the base, which was formed very readily, could not be degraded by the usual Hofmann method, but regenerated the original phenolic base on treatment with caustic soda. This clearly indicates the presence in the molecule of a phenol-betaine ring which alone could account for the observed change. The significance of this reaction will be best understood from the following scheme :

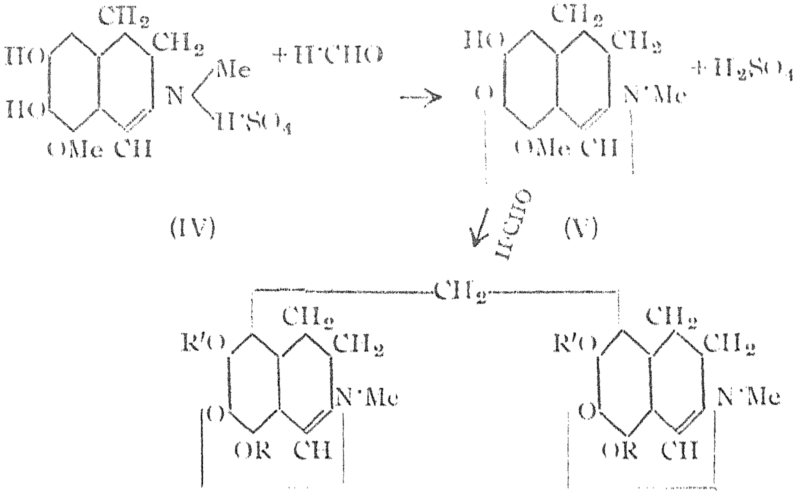


Similarly, the methiodide of the methoxy compound reacted with alkali regenerating the free methoxy base.

The foregoing experimental facts together with Freund's interpretation of the action of sulphuric acid on hydrocotarnine (*loc. cit.*) have made it possible to arrive at an understanding of the mechanism of the formation of this base from cotarnine under the influence of sulphuric acid.

In acid medium cotarnine changes from the aldehydeimino form (II) to the ammonium form (III), the latter being gradually demethylenated by sulphuric acid into an intermediate phenolic body (IV) and formaldehyde. The loss of sulphuric acid from (IV) results in the formation of a compound with a betaine ring (V). The reaction does not, however, end here, but the formaldehyde split off in the reaction subsequently condenses with (V) at the reactive 5-position and forms methylene-bis-phenol-betaine of 2-methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro*iso*quinolinium hydroxide (VI).





(where R = Me, R′ = H). (VI)

The methylene dicotarnine structure (VI) for the new base has been based mainly on the ground that it forms definitely both a mono- and a dinitrate and that the molecular weight of its methyl ether corresponds to the dimolecular formula. The molecular weight of the phenolic base could not be determined satisfactorily on account of its sparing solubility in all ordinary solvents and in camphor. The phenolic base gives only a monomethiodide and a monoethiodide while the methylated base forms the normal dimethiodide. The difference which may be due to steric factors is difficult to explain. Freund and Reitz (*Ber.*, 1909, **39**, 2233) who made a similar observation with *bis*hydrocotarnine expressed the view that the combination of the dimolecular base with only one molecule of methyl iodide should be attributed to steric hindrance. Another presumptive evidence in favour of the dimolecular formula of the new base is to be found in the sparing solubility of all its salts with mineral acids. The salts of cotarnine and hydrocotarnine and their simple derivatives with mineral acids are all very soluble in water, while those of *bis*hydrocotarnine, methylene dicotarnine, nitrobenzoyl and nitrobenzylidene cotarnine and all similar bases having a high molecular weight are, as a rule, found to be characterised by their sparing solubility.

Many attempts have been made to place the formula on unassailable ground by oxidising the base and obtaining a product of known structure, but without success.

EXPERIMENTAL.

Methylene bis-*phenol-betaine of 2-Methyl-6:7-dihydroxy-8-methoxy-3:4-dihydroisoquinolinium Hydroxide* (VI, R=Me, R′=H) (compound A).

Cotarnine (5 g.) was dissolved in ice-cold 90 % sulphuric acid (15 c.c.) and the mixture left for 3 days at room temperature. The solution which acquired a deep scarlet colour was then poured into ice-water and basified with ammonia. The yellow crystalline precipitate, that gradually separated out, was filtered after 2 hours and dried on a plate. The crude product weighed 4·0 g., m. p. 302°-304°. It was crystallised from a large excess of boiling alcohol as glistening dark yellow needles, m.p. 308° (decomp.), yield 3 g. [Found (in a sample dried in vacuum over quicklime for 24 hours) : C, 62·13; H, 6·25; N, 6·71; OMe, 13·45; H_2O (on heating over P_2O_5 at 110°/5 mm.), 3·40. $C_{23}H_{26}O_6N_2$, H_2O requires C, 62·16; H, 6·30; N, 6·31; OMe, 13·96; H_2O 4·05 per cent].

It is sparingly soluble in alcohol, chloroform and acetone, insoluble in benzene and ether and readily soluble in hot aniline.

The *Dihydrochloride* was prepared by adding a few drops of concentrated hydrochloric acid to a suspension of the base in absolute alcohol. The clear solution which resulted very quickly deposited light yellow needles, m.p. 200° (decomp.). [Found (in air-dried substance): Cl, 13·20. $C_{23}H_{26}O_6N_2$, 2HCl requires Cl, 14·22 per cent].

The *Dihydrobromide* was prepared in the same manner. It crystallised from alcohol in colourless needles, m. p. 212° (decomp.). (Found: Br, 26·71. $C_{23}H_{26}O_6N_2$, 2HBr requires Br, 27·20 per cent).

The *Mononitrate*.—The base (0·5 g.) was dissolved in *N*-HNO_3 (1 c.c.). The clear solution on standing deposited light yellow needles. It was recrystallised from hot water as colourless fibrous needles, m.p. 222°. (Found: N, 8·49. $C_{23}H_{27}O_9N_3$ requires N, 8·58 per cent).

The *Dinitrate* was prepared by treating the base (0·5 g.) with *N*HNO_3 (2 c.c.). The clear solution on standing deposited light yellow needles. This was very soluble in water but could be recrystallised from absolute alcohol as needles, m. p. 93°. (Found: N, 9·90. $C_{23}H_{28}O_{12}N_4$ requires N, 10·14 per cent).

The *Platinichloride* came down in orange-red plates on adding chloroplatinic acid to a solution of the base in concentrated hydrochloric acid, m. p. 198° (decomp.). [Found: H_2O (at 110°-120°), 2·09. $C_{23}H_{26}O_6N_2$, 2HCl, $PtCl_4$, H_2O requires H_2O, 2·09 per cent.]. The anhydrous salt was analysed for platinum. [Found Pt, 23·01. $C_{23}H_{26}O_6N_2$, 2HCl, $PtCl_4$ requires Pt, 23·23 per cent].

The *Dipicrate* was prepared by adding excess of saturated aqueous picric acid solution to a solution of the base in very dilute hydrochloric acid. It separated from alcohol as stout, straw-yellow prisms, m. p. 230° (decomp.). (Found: N, 11·02. $C_{35}H_{32}O_{20}N_8$ requires N, 12·66 per cent).

The *Monomethiodide* was prepared by heating the components in a pressure bottle at 100° for 2 hours and recrystallising the dark yellow product from hot water. It formed straw-yellow rectangular plates, m. p. 220° (decomp.). [Found: C, 49·23; H, 5·38; N, 5·02; H_2O (at 110°/5mm over P_2O_5), 3·42. $C_{24}H_{29}O_6N_2I$, H_2O requires C, 49·14; H, 5·29; N, 4·77; H_2O, 3·05 per cent].

Action of Caustic Soda on the Monomethiodide:—The monomethiodide (1 g.) was dissolved in 2*N*-caustic soda (20 c.c.) and the solution heated on the steam-bath for half an hour. The solution was then cooled in ice and acidified with dilute hydrochloric acid and ammonia was added till the solution was faintly alkaline. On standing yellow crystals separated out. These were filtered and recrystallised from alcohol as yellow needles, m.p. 308°, not depressed by admixture with (VI, R′=H, R=Me). The hydrochloride, the picrate and the methoxy derivative of this product were identical with the hydrochloride, the picrate and the methoxy derivative of the parent base. The yield of the regenerated base was 0·6 g.

The *Monoethiodide* was prepared in the same manner. It crystallised from hot water in rectangular plates, m. p. 222°. The substance was dried at 110°/5 mm. for analysis. (Found: I, 21·44. $C_{25}H_{31}O_6N_2I$ requires I, 21·82 per cent).

Demethylation with HI. *Formation of Methylene-bis-phenol-betaine of 2-methyl-6:7:8-trihydroxy-3:4-dihydroisoquinolinium Hydroxide* (VI, R′=H, R=H).

The base (1 g.) and freshly distilled hydriodic acid (5 c. c.) were heated together in a sealed tube at 130°-140° for 5 hours. The excess of hydriodic acid was distilled off and the dark periodide was left in contact with sulphurous acid for 2 hours. The hydroiodide gradually separated out in light yellow needles. Recrystallisation from hot water gave bright yellow needles, m. p. 220° (decomp.). The free base was obtained by decomposing the salt with ammonia and crystallising the yellow precipitate from a large excess of boiling alcohol as dark yellow needles, m. p. 275° (decomp.). [Found (air-dried sample): I, 39·61. $C_{21}H_{22}O_6N_2$, 2HI requires I, 38·83 per cent].

The *Dinitrate* was obtained as a crystalline precipitate by rubbing the base with a few drops of dilute nitric acid. It was recrystallised from hot water as colourless fibrous needles, m. p. 195° (decomp.).

*Methylation with Dimethylsulphate. Formation of Methylene*bis-*phenol-betaine of 2-Methyl-6:8-dimethoxy-7-hydroxy-3:4-dihydro* iso-*quinolinium Hydroxide* (VI, R′=Me R=Me) (Compound B).

The base, m.p. 308°, (2 g.) was dissolved in 2 *N*-caustic soda (10 c.c.), dimethyl sulphate (2 c.c.) was added and the mixture vigorously shaken. The methoxy compound separated out quickly as a light yellow crystalline precipitate, which was filtered, washed with cold water and recrystallised from hot water as long yellow needles, m.p. 268° (decomp.), yield 1·6 g. [Found: C, 66·06; H, 7·04; N, 5·88; OMe, 26·7; M.W. (Rast method), 418·4. $C_{25}H_{30}O_6N_2$ requires C, 66·08; H, 6·60; N, 6·16; OMe, 27·31 per cent. M.W., 454·0].

The identical compound was obtained when a mixture of the base (1 g.) dissolved in dilute caustic soda (4 c.c.) and excess of methyl iodide was heated in a pressure bottle at 100° for 1 hour. On cooling yellow crystals separated out. These were filtered and recrystallised from hot water as yellow needles melting at 268° (mixed m.p.).

The mother liquor from the above on acidification threw down a yellow precipitate of the methiodide which crystallised from hot water in yellow needles, melting at 180° (mixed m.p.) (*vide infra*).

The *Dihydrochloride* was prepared by treating a suspension of the above base in water with dilute hydrochloric acid. The hydrochloride crystallised from hot water in clusters of needles, m.p. 191° (decomp.). [Found (in a sample dried at 110-20°): Cl, 12·72. $C_{25}H_{30}O_6N_2$, 2HCl requires Cl, 13·47 per cent].

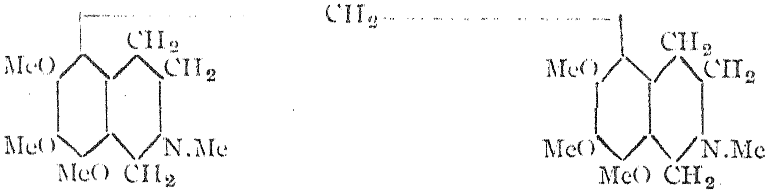
The *Dinitrate*, prepared in the usual manner, crystallised from hot water in fibrous needles, m.p. 235° (decomp.). (Found: N, 9·49. $C_{25}H_{30}O_6N_2$, $2HNO_3$ requires N, 9·65 per cent).

The *Platinichloride* came down as orange-red plates, m.p. 248° (decomp.). The *picrate*, prepared in the usual manner, crystallised from alcohol in yellow prisms, m.p. 114°.

The *Dimethiodide* crystallised from hot water in long yellow plates, m.p. 180° (decomp.). (Found: I, 33·96. $C_{27}H_{36}O_6N_2I_2$ requires I, 34·42 per cent).

Action of Caustic Soda on the Methiodide.—The methiodide (1 g.) was dissolved in warm 2*N*-caustic soda (4 c.c.) and the solution heated to 60° on the water-bath for ½ hour. The clear solution, on standing, deposited yellow needles. These were collected and recrystallised from hot water as bright yellow needles, m.p. 268°, not depressed by admixture with (VI, R′ = Me, R = Me).

Action of Nascent Hydrogen on the Methiodide of Compound B. Formation of Methylene-bis-2-methyl-6:7:8-trimethoxy-1:2:3:4-tetrahydro-isoquinoline.



The methiodide of the base B (0·5 g.) was treated with 4N-H_2SO_4 (10 c.c.) and zinc dust (1 g.), and the mixture was heated on the water-bath. The solution which was at first yellow gradually became colourless in about 10 minutes and after heating for another 30 minutes, the solution was filtered from the excess of zinc, cooled strong ammonia added and the liquid extracted thrice with ether. The ether solution dried over anhydrous K_2CO_3 and the ether distilled off. The crystalline residue was recrystallised from alcohol as colourless prisms, m.p. 201°. (Found: C, 66·05; H, 7·51. $C_{27}H_{38}O_6N_2$ requires C, 66·67; H, 7·81 per cent).

SUMMARY.

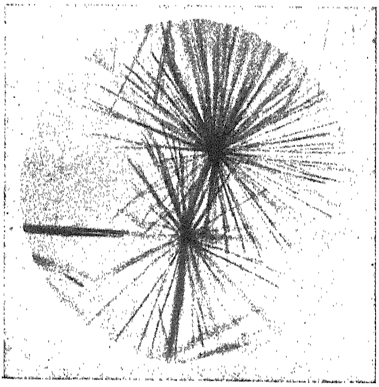
Cotarnine, in the presence of 90% sulphuric acid, undergoes a deep-seated change. The acid is supposed first to demethylenate the base, formaldehyde and a phenolic body (2-methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro-*iso*quinolinium sulphate) being formed. The latter loses sulphuric acid and a phenolic compound with a betaine ring (phenol-betaine of 2-methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro-*iso*quinolinium hydroxide) is formed. The formaldehyde, split off in the reaction, then condenses with the 'phenol-betaine compound' at the reactive *ana*-(5-) position, forming methylene-bis-phenol-betaine of 2-methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro-*iso*quinolinium hydroxide.

The analyses of the new base, its methyl ether, their salts and their methiodides have been found to be in complete harmony with the above constitution for the base.

PRESIDENCY COLLEGE,
MADRAS.

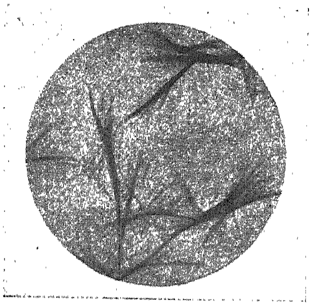
Received April 7, 1936.

Fig. 1



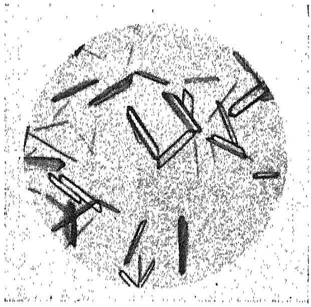
Methylene-*bis*-phenol-betaine of 2-methyl-6 : 7-dihydroxy-8-methoxy-3 : 4-dihydro*iso*quinolinium hydroxide (Compound A).

Fig 2



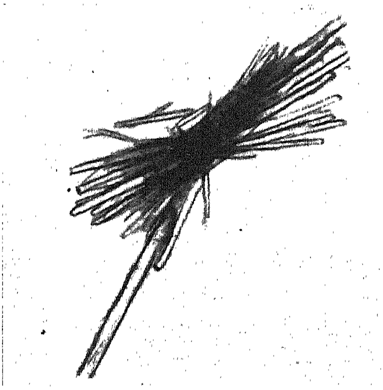
Mononitrate of Comp. A

Fig. 3



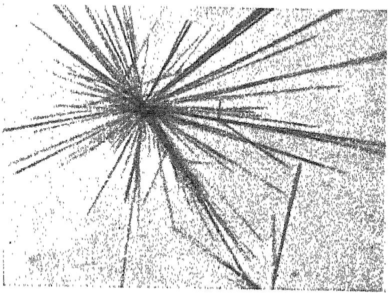
Platinichloride of Comp. A.

Fig. 4



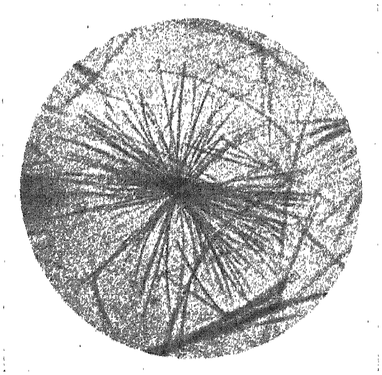
Monomethiodide of Comp. A

Fig. 5



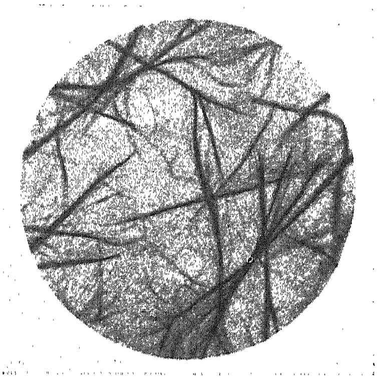
Methylene-*bis*-phenol-betaine of 2-methyl-6 : 8-dimethoxy-7 hydroxy-3 : 4-dihydro*iso*quinolinium hydroxide (Compound B).

Fig. 6



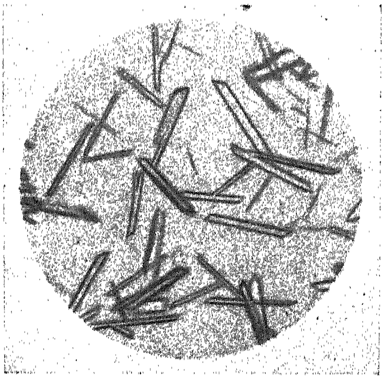
Dihydrochloride of Comp. B.

Fig. 7



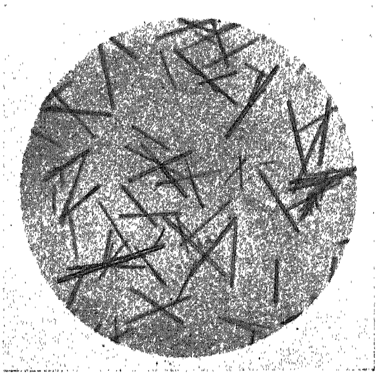
Dinitrate of Compound B.

Fig. 8

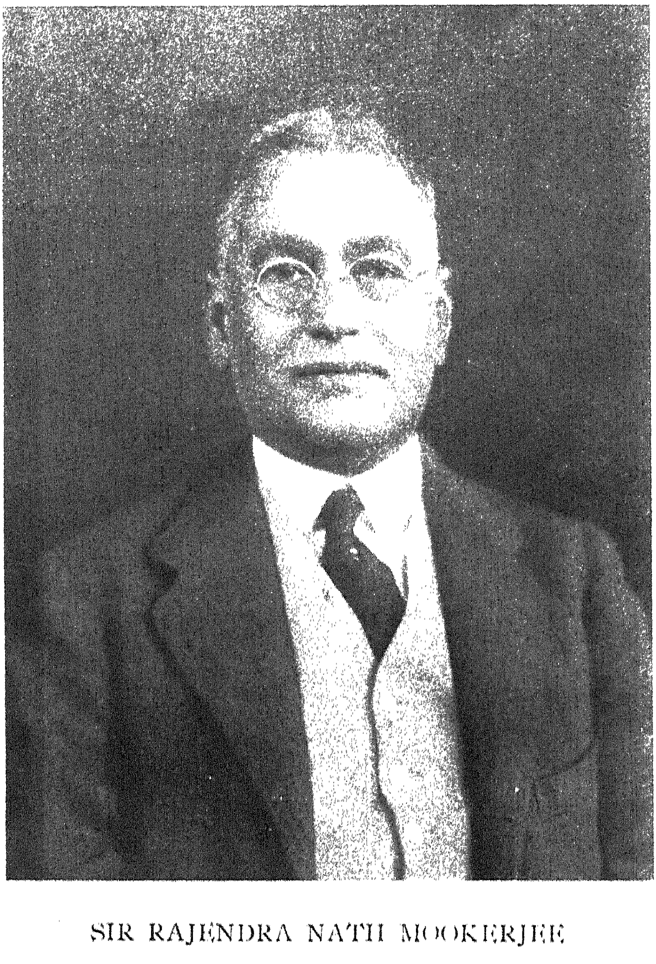


Platinichloride of Compound B.

Fig 9



Dimethiodide of Compound B.



SIR RAJENDRA NATH MOOKERJEE

Obituary

SIR RAJENDRA NATH MOOKERJEE

Born, June 23, 1854. Died, May 15, 1936.

By the death of Sir Rajendra Nath Mookerjee, the Indian Chemical Society has lost one of its patrons. The Society had the privilege of enjoying his patronage since its inauguration. His keen interest in the progress of science in India was a source of strength and inspiration to many scientific institutions.

Sir Rajendra Nath was born on June 23, 1854, in the village of Bhabla in 24 perg. (Bengal). He started his career as a contractor on partnership basis with an Indian firm and owed his advancement to nothing but his own merit and capacity for real hard work. The phenomenal success in his business enterprise is indeed a tale of romance and unique in Bengal. From the position of an engineer in the firm of Messrs Martin & Co. he lived to become the senior partner of the concern and gradually became the head of the biggest engineering combine comprising of Martin & Co., Burn and Co., Indian Iron & Steel Co., and the Indian Standard Wagon Co.

Beneficient activities of Sir Rajendra Nath were not confined to business alone and overflowed in various directions. His services were continually sought by the State and freely given. He was a true nationalist without sharing recognised creeds of any of the political parties. As a mark of appreciation of his abilities and services to the country, the title of C.I.E. was conferred on him by the Government and he was made a "Captain of Industry in Bengal" in 1909, and subsequently a K.C.I.E., in 1911. He was honoured with a K.C.V.O., in 1922.

He held the office of Sheriff of Calcutta about 25 years ago and during 1916-18 became the Chairman of the Industrial Commission. He was the President of the Bengal Retrenchment Committee, appointed by Lord Lytton and was member of most of the important Industrial Committees and Commissions appointed by the State. He presided over Industrial Conference at Allahabad in 1910 and delivered the annual convocation address of the Patna University in 1919. Sir Rajendra Nath Mookerjee was elected General President of the Indian Science Congress in 1921 and was the Chairman of its Reception

Committee in Calcutta in 1928. He was President of the Asiatic Society of Bengal in 1924 and a Fellow of the Calcutta University for many years. He also held the office of president of the Indian Association for the Cultivation of Science. Sir Rajendra Nath was a man of strong conviction and character with a dynamic personality.

PROF. RAJENDRA NATH SEN

Born, 1878 Died, May 9, 1936.

By the unexpected death of Professor Rajendra Nath Sen at his residence in Calcutta on May 9, the Indian Chemical Society has lost one of its Foundation Fellows and an ardent supporter of the cause of the Society. Prof. Sen was elected an ordinary member of the Council at the inception of the Society and served the Council in various capacities at different periods. He filled the office of Hony. Treasurer during 1928-1930, served the publication Committee as its member during 1931-32 and was an ordinary member of the Council again since 1935 till his demise.

Prof. Sen was born in Calcutta in 1878 and was educated in the Albert School and Presidency College, where he graduated with triple honours in Chemistry, Physics and Mathematics in 1897 and stood first in M.A. Examination in Physics in the next year.

He began his teaching career as Professor of Physics first at Uttarpara College, Hooghly, for three years and subsequently at Jagannath College, Dacca. He went to England in 1906 and devoted his attention to the study of synthetic dyes at the University of Leeds under the guidance of Prof. Arthur Green, and obtained the M.Sc. degree of that University. During his stay for three years at the Leeds University he carried out a number of investigations and published sometime later four independent papers in the Journal of the Society of Dyers and Colourists and two papers in collaboration with Prof. Arthur Green in the Journal of the Chemical Society.

On his return to India in 1909, Mr. Sen was appointed as Professor of Tinctorial Chemistry, a newly created department in the Sibpur Engineering College, where he stayed till 1915. In 1916 Prof. Sen was appointed Chief Chemist, Govt. Test House, Alipore, where he stayed for three years. In 1919 he joined the Presidency College as Professor of Chemistry and found the atmosphere congenial to his aptitude for chemical research and devoted himself in collaboration with his students to original investigations in

PROF. RAJENDRA NATH SEN

the chemistry of synthetic dyes and published a fairly large number of papers, an account of which has been given later. Apart from the investigations of synthetic dyes he published several papers on the chemistry of natural products. After his joining the Presidency College, the first paper that appeared in his name, linked with that of Col. K. K. Chatterji, was chemical composition of Nim or Margosa oil.

In 1934 he was transferred from the Presidency College to Krisnagore as Principal of the Govt. College at that place and retired from that post in December 1934. Prof. Sen was a man of strong principles and of very simple habit. His sweet temper and purity of character endeared him both to his students, colleagues and friends alike.

Apart from his usual duties as teacher and research worker, he took an active interest in the industrial development of the countries' resources and was one of the founders of the well-known Calcutta Chemical Co., Ld. He undertook cheerfully the onerous duties of the Hony. Treasurer of the Society and continued in the office for three years till his transfer from Calcutta.

Below is given an account of various papers published by Prof. R.N. Sen himself and with his collaborators.

1. Suggested Method for a Rapid and sufficiently exact Estimation of Sodium Sulphide in a standing bath of Sulphide Dye. (*J. Soc. Dyers & Colour.*, August 1914, **30**, No. 8);

2. Black Dyeing on Tussur Silk. (*ibid.*, 1916, **32**, No. 10).

3. Production of Aniline Black on Wool. (*ibid.*, No 10).

4. Dyeing of Wool with the Sulphide Colour. (*ibid.*, No. 10).

5 With K.K. Chatterji—Chemical Composition of Nim or Margosa Oil. (*Indian J. Med. Res.*, 1920, **8**, N. 2),

6. With Arthur George Green—Azo-dyestuffs of the Triphenylmethane Group. (*J. Chem. Soc.*, 1912, **101**, 137).

7. Azomethineazo-dyes. (*ibid.*, 1910, **97**, 2242).

8. With Balaram Sett—Studies in Dyes with Multiple Chromophores. (*J. Amer. Chem. Soc.*, 1924, **46**, 1913).

9. With Nripendra Nath Sinha—Condensation of Aldehydes with Resorcinol and some other Aromatic Hydroxy Compounds. (*ibid.*, 1923, **45**, 2986).

10. With K.K. Chatterji and S.N. Datta—Preliminary Study and Chemical Examination of the Seeds of *Buchki*. (*Indian J. Med.*, 1923, September No.).

11 With Sarbbani Sahaya Guha-Sircar—The Condensation of Resorcinol and a few other Aromatic Hydroxy Compounds with some Acids, Esters, Lactones and Lactams. (*J. Indian Chem. Soc.*, 1924, **1**, 153).

12. With Nripendra Nath Sinha and Nripendra Nath Sarkar—The Condensation of Chloroform, Carbon Tetrachloride and Iodoform with Resorcinol and similar other Hydroxy Aromatic Compounds. (*ibid.*, 1925, **1**, 303).

13. With Nripendra Nath Srakar—The Condensation of Primary Alcohols with Resorcinol and other Hydroxy Aromatic Compounds. (*J. Amer. Chem. Soc.*, 1925, **47**, 1079).

14. With Benoybhusan Ghosh—Azo-triphenylmethane and Azo-pyronine Dyes (*Meta* series). (*J. Indian Chem. Soc.*, 1928, **5**, 487).

15. With Duhkhaharan Chakravarti—Alkali Sulphonates of Coumarin and Nitrocoumarin. (*ibid.*, 1928, **5**, 433).

16.—6-Aldehydo-coumarin and Dyes derived from it. (*J. Amer. Chem. Soc.*, 1928, **50**, 2328).

17.—Mercuration of Coumarins. (*J. Indian Chem. Soc.*, 1929, **6**, 847).

18.—Coumaro-pyrones. (*ibid.*, 1929, **6**, 793).

19. With Asutosh Mukherji—The Condensation of Esters with Resorcinol, Dimethylaniline and Diethyl-*m*-aminophenol. (*ibid.*, 1929, **6**, 557).

20. With Kanakendra Narayon Banerjea—Aldehydofluorescein and Dyes derived from it. (*ibid.*, 1929, **6**, 367).

21. With Suresh Chandra Sen-Gupta—Studies in the Condensation of Di-*ortho*-thiobenzoic Acid with Aromatic Hydroxy Compounds. (*ibid.*, 1929, **6**, 367).

22. With Kali Charan Kar—Aldehydo-phenolphthalein and Dyes derived from it. (*ibid.*, 1929, **6**, 53)

23. With Nalin Chandra Chattopadhaya and Suresh Chandra Sen-Gupta—The Condensation of Ketones with Resorcinol. Part II. (*ibid.*, 1930, **7**, 997).

24. With Bholanath Sen—Triphenylmethane Dyes derived from Quinoline, Tetrahydroquinoline and Carbazole. (*ibid.*, 1930, **7**, 965).

25. With Biresh Chandra Roy—Condensation of Levulinic Acid with Aldehydes. (*ibid.*, 1930, **7**, 401).

26. With Asutosh Mukherji—Condensation of Urethane, Phenylurethane and Diphenylurethane with Resorcinol. (*ibid.*, 1930, **7**, 275).

27. With Duhkhaharan Chakravarti—A new Method of Conversion of Coumarins to *o*-Coumaric Acids. (*ibid.*, 1930, **7**, 247).

28. With Muhammad Qudrat-i-Khuda—The Condensations of Ketones with Resorcinol. Part I. Condensation by Addition. (*ibid.*, 1930, 7, 167).

29. With Akshoy Kumar Sen—Studies in Azotriphenyl-carbinol Dyes. (*ibid.*, 1930, **7**, 151).

30. Studies in Azomethine-azo Dyes. (*ibid.*, 1930, p. 11).

31. With Sudhansukumar Banerjee—Studies in Tetraphenylmethane Derivatives. Nonquinonoid Dyes. Part I. (*ibid.*, 1931, 8, 77).

32. With Ganapati Banerjee—The Bitter Principle of Neem Oil. Part I. (*ibid.*, 1931, **8**, 773).

33. With Sarajendu Dutt—4 : 4′-Dihydroxydiphenyl-3 : 3′-dialdehyde and its Derivatives. (*ibid.*, 1931, p. 223).

34. With Jatindralal Nandi—Condensation of Dibenzylketone with Aromatic Aldehydes and Ketones. (*ibid.*, 1931, p. 591).

35. With Susil Kumar Ray—Studies on Riemer-Tiemann Reaction. (*ibid.*, 1932, **9**, 173).

36. —— Condensation of Benzotrichloride with Phenols. (*ibid.* 1932, p. 181),

37. With R. Sadasivam—Studies on the formation of Aozxy, Azo, Hydrazo and Benzidine Compounds and the Dyes derived from the latter. (*ibid.*, 1932, p. 403).

38. With Gopal Chandra Mukherjee— 6-Aldehydo-4-methyl-α-naphthapyrone and Dyes derived from it. (*ibid.*, 1933, **10**, 271).

39. —— Antimony and Mercury Compounds of Quinoline and *iso*Quinoline. (*ibid.*, 1934, **11**, 541).

40. With Manas Mohan Ghosh—Studies in Tetraphenylmethane Dyes. Part II. (*ibid.*, 1934, p. 455).

41. With Sachindra Nath Roy—Azotriphenylmethane and Azopyronine Dyes. (*ibid.*, 1934, p. 21).

42. With Bijonkumar Sen—Condensation of Pyruvic acid with Aldehydes. (*ibid.*, 1934, p. 411).

43. With B. N. Banerji—Studies on Azo-aldehydes. (*ibid.* 1935, **12**, 295).

Review

Schwimmaufbereitung—(Wissenschaftliche Forchungsberichte—Naturwissenschaftiiche Reihe—Herausgegeben von Dr. R. E. Liesegang. Band XXXVI.) VON W. PETERSON; VERLAG VON THEODOR STEINKOPF. Pp. 337 + XII; Price. R. M. 19·50.

Minerals and ores occur in nature mixed with earthy materials and worthless other metallic compounds. The concentration in the ore of the desired metallic compounds is effected by various methods other than the metallurgical and chemical treatments, by which former methods the chemical nature of the compounds remain unchanged. These preparatory treatments may be classified as (*i*) Gravitational—depending on different specific gravities of the constituents of the ores, (*ii*) Magnetic—depending on different magnetic properties, (*iii*) Flotation methods—dependent on different covering power of water on the constituents of the ore. Generally water has less covering power on the desired metallic compounds of the ore, which is still further cut down by the addition of certain organic compounds in very small quantities to the turbid mixture of water and the finely subdivided (generally of less than 0·3 mm. diam.) ore. The turbid mixture is kept under constant stirring and air or in some cases carbon dioxide is blown in very fine bubles and the gas adheres to the water-free surface of the ore-particles which thus enveloped with gas acquire diminished average specific gravities and float to the surface in the form of scum or froth and the gangue with unchanged specific gravity sinks to the bottom. The reverse may also happen and the gangue may float to the surface and the desired ore sink to the bottom. In any case the separation is affected by formation of the scum or forth.

The burden of the book under review is to decribe the various steps taken for the preparation of the froth and to discuss the theoretical principles involved in the selection of the organic and inorganic compounds mentioned above and the mechanism of the formation of the froth or scum. The importance of the flotation-process may be gauged from the fact that the total amount of ores thus treated per year all over the world is about 120 million tons. In the U. S. A. alone, for which reliable and accurate figures are available from the Bureau of Mines, in the year 1928, 69·7 million tons of the ore treated by this method yielded 4·16 million tons of concentrates. In India the only place, where to our knowledge, the process has found application is at Ghatshila (B. N. R.) in the works of the Indian Copper Corporation. The method is applied, only on the European Continent, for the recovery of coal from coal-washings and coal-dust.

In most cases the art comes before the science; here as well the flotation process was applied in a crude form by the Arabs in the 15th. century but found intensive and varied application in the concentration of metallic ores and graphite since the middle of the last century. It is only lately that attempts are being made to explain the phenomenon on theoretical grounds. No one single theory *e.g.*, electrostatic theory, surface-tension theory, adsorption theory, etc., can satisfactorily explain the whole phenomenon. The variables involved are so numerous that principles of Physics, Chemistry, Colloid Chemistry, Mineralogy, etc., must be simultaneously taken into consideration to get satisfactory results.

Up to now this is one of the few comprehensive treatises on the subject, the other one, in the English language, being "Flotation Plans Practice" by Rabone. The book is divided into 22 chapters besides index, complete bibliography of all references (856 in all), cost of materials, etc.

The materials required for bringing about the froth are classified by the author under the following heads:—

(i) Froth-producers (Schaumer)—Such as polar-nonpolar organic compounds of moderately large molecular weights—pine oils, aniline, *o*-toluidine, xylidine, ethyl alcohol, butyl alcohol, etc.—amounts used vary from 20 to 200 gms. per ton of ore.

(ii) Collectors or Combiners (Sammler)—These are organic substances of polar-nonpolar molecular structure which by chemical reaction, chemosorption or pure adsorption on the surface of the ore particles render the latter hydrophobe and more difficultly coverable by water than would otherwise be the case in the froth. The polar part of the molecule is directed towards the surface of the ore-particle and water is kept away—Creosote oil, coal tar, ethyl-, butyl-, amyl-xanthate, sodium dicresyldithioxanthate, phosphorus pentasulphide, naphthylamine, etc. etc—amounts required are a few gms. per ton of ore.

(iii) Regulating swim—, or suspension-agents:

(a) Depressing suspension-agents. The common property of all such agents is the ability to render the minerals to be precipitated

hydrophil and polar so that they may not remain in suspension and float to the surface with the froth. So these agents are generally strong electrolytes and are chosen according to their precipitating capacities for the constituents under consideration.

(*b*) Restorative swim-, or suspension-agents. These agents may also restore the swimming capacity of particles precipitated by the depressing suppression-agents, or increase the swimming capacity of the previously untreated particles. Generally sulphates, phosphates and some nitrates are used, but copper sulphate has found the widest application.

Besides these there are substances presence of which robs the particles of their swimming capacity, and there are antidotes for these "poisons" as well.

The author has tried his best to explain the phenomena as a whole and the action of the various agents used. But in the absence of quantitative data the explanations given can, at best be considered as only tentative. The book, because of the vast amount of data, will be of great help to the scientists engaged in actual operations and will be of interest to the physical chemists for carrying on further work on the lines suggested for obtaining quantitative results, if possible.

Most treatises on individual industrial processes suffer from one common defect, namely, the assumption by the authors of almost complete ignorance of physics and physical chemistry on the part of their readers. Without this assumption this book could have been reduced to about half of its present bulk.

H. L. R.

Chemical Examination of the Fixed Oil from the Seeds of *Celastrus Paniculatus* Willd.

O. N. KUMARASWAMY AND B. L. MANJUNATH.

Celastrus Paniculatus, a shrub of the natural order *Celastrineæ*, is found in Bihar, Bengal, Burma and Ceylon (Kanny Lall Dey, "The Indigenous Drugs of India," 1896, p. 74; Nadkarni, "The Indian Materia Medica" 1927, p. 187). Its seeds yield an oil "said to be a sovereign remedy in beri-beri, and a stimulant." In Ayurvedic and Unani Medicines use of the seeds and of the oil is recommended in rheumatism, gout, paralysis and leprosy (*cf.* Nadkarni, *loc. cit.;* Chopra, "The Indigenous Drugs of India," 1933, p. 473.). The oil is reputed to be a nerve-stimulant and a brain-tonic. Since very little work has been done on the oil, the following investigation was undertaken.

EXPERIMENTAL.

50 G. of the crushed seeds were extracted with the following solvents successively in a soxhlet:

	Extract.
Petroleum ether (b. p. 50—60°)	52·2 %
Ethyl ether	1·6
Chloroform	0·5
Ethyl acetate	0·4
Alcohol	2·8
	57·5

The petroleum ether extract gave a thick brownish yellow oil with an unpleasant taste. The other extracts consisted of highly coloured viscous materials about which no definite conclusions could be drawn.

Though the occurrence of an alkaloid in the seeds is mentioned in the literature (Wehmer, "Die pflanzenstoffe," 1931, p. 717; Chopra, *loc. cit.*), no satisfactory evidence for it was obtained when the seeds were tested with Prollius fluid. 300 G. of the seeds were subjected to steam distillation, and the steam-volatile matter was found to be 0·015%. This material was a dark brown solid with a strong odour resembling that of the oil-cake. The aqueous extracts of the seeds contained traces of tannins and of reducing sugars, but no starch. The amount of reducing sugars did not increase on acid hydrolysis.

Fatty Oil.

The fatty oil was extracted by petroleum ether (b. p. 50—60°) and the purified material had the following constants.

Specific gravity 25°/25°	0·9586
Refractive index at 30°	1·4747
Saponification value	239·2
Acid value	44·4
Iodine value (Hanus.).	102·9
Reichert-Meissl value	62·8
Acetyl value	130·1
Unsaponifiable matter	5·7%
Hehner value	75·2%

Mixed Fatty Acids.

2 Kg. of the oil were saponified, and the acids that were liberated, were reconverted into sodium soap. This, in the form of dry shavings, was extracted with ether in a soxhlet to obtain the unsaponifiable matter. The fatty acids were next set free, and a purified sample was found to have the following constants.

Mean mol. wt. of the mixed fatty acids	275·3
Iodine value ,, ,, (Hanus)	112·6
Solid or saturated acids (Twitchell's method)	30·54%
Liquid or unsaturated acids ...	68·48%

The mixed fatty acids were resolved into their saturated and unsaturated components by Twitchell's lead salt method (*Ind. Eng. Chem.*, 1921, **13**, 806). During the process a small amount of a brown resinous substance separated out. The saturated and the unsaturated acids obtained had the following constants.

	Mean mol. wt.	Iodine value (Hanus.).
Solid acids	264·0	1·8
Liquid acids	335·7	154·9

Liquid Fatty Acids.

The liquid acid mixture was esterified with methyl alcohol, and the ester (283 g.) was distilled at 1 mm. pressure. The bulk of the distillate (240 g.) passed over between 170°—180° and had mean mol. weight 277·7 and iodine value 166·2.

A portion of the acid (4 g.) obtained by saponification was treated with bromine according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils and Fats," 1913, Vol. I, p. 573). 1·7 G. of a dull white ether-insoluble bromo compound separated. This material dissolved completely in benzene and on purification gave hexabromostearic acid (m. p. 181·5; M.W., 757), indicating the presence of linolenic acid. From the filtrate no tetrabromostearic acid could be isolated.

Another portion of the liquid acid mixture (15 g.) was oxidised by cold dilute alkaline permanganate. From the mixture of hydroxy acids so formed the following were isolated.

Acids.	M. p.	M. W. (found.)	M. W. calculated.
Dihydroxystearic	131°	316·2	316·4
Tetrahydroxystearic	(*a*) 154°—155°	347·2	
	(*b*) 167°—168°	346·2	348·4
	(*c*) 171°	351	
Hexahydroxystearic	(*a*) 166°	376·9	380·4
	(*b*) 194°	379·8	

Thus the occurrence of oleic, linoleic and linolenic acids among the unsaturated acids is established.

Solid Fatty Acids.

The solid acid mixture, obtained above, was slightly coloured. It was esterified with methyl alcohol. 394 G. of the mixed esters were distilled under a pressure of 1 mm.

The major portion of the distillate A (319 g.) came over at 153°-158°. The rest B (67 g.) was collected at 158-165°. The residue in the flask including loss amounted to 8 g. A consisted entirely of methyl palmitate (M.W. of acid from saponification value, 258·7). From this palmitic acid (m.p. 61·5-62°; M.W., 258·4) was obtained in quantitative yield. The acid from the residues after careful purification and recrystallisations from ethyl acetate melted at 78° (M.W. 393), and it did not depress the melting point of pure cerotic acid (m.p. 78°; M.W. 396.).

Fraction B was again subjected to careful refractionation at a pressure less than 1 mm.

Fraction.	Temp. range.	Weight.	M. W. of acid from the saponification value.
I	158-162°	29 g.	264·6
II	162-170°	16	270·4
III	170-178°	11·5	276·8
IV	178°	3·5	278·9
V	Residue including loss.	7	—

Fraction I.—This gave an acid which corresponded to an eutectic mixture of palmitic and stearic acids. Repeated crystallisations from various solvents gave a product melting at 56-57° (M.W. 268).

Fractions II *and* III.—The crude acids from these after repeated crystallisations from alcohol yielded pure stearic acid (m.p. 69·5-70°; M.W., 284·3). Its *p*-phenylphenacyl ester melted at 97·5°.

Fraction IV.—The acid liberated from this fraction, after a few crystallisations, melted at 62° (M.W., 296), and could not be examined further.

Fraction V.—This was saponified, and the acid liberated after repeated crystallisations from ethyl acetate melted at 76° and had M.W. 370·6. Its *p*-phenylphenacyl ester melted at 100°. It is, therefore, to be regarded as crude lignoceric acid.

Volatile Acids.

Since the Reichert-Meissl value for the oil was found to be unusally high, the nature of the volatile acids present was examined.

250 G. of the oil were saponified with alcoholic potash and the

alcohol was distilled over. The aqueous solution of the soap was acidified with sulphuric acid and the resulting mixture was subjected to steam distillation till the distillate contained hardly any trace of acid. The distillate was neutralised with potassium hydroxide and evaporated to a small volume. On acidifying this with sulphuric acid and cooling a mass of brownish flakes appeared. This was separated, dissolved in alcohol and boiled with animal charcoal and filtered. The crystalline material, that separated out, was recrystallised from boiling water, when it was obtained in colourless glistening plates, m.p. 121° (M.W. 122), and it was found to be benzoic acid (m.p. of *p*-phenylphenacyl ester, 167-68°).

After the separation of benzoic acid, the aqueous solution was treated with some more sulphuric acid and again subjected to steam distillation. The distillate was neutralised with litharge and the solution was evaporated to dryness. The lead salt thus obtained was dried at 120° and decomposed at 150° by dry hydrogen sulphide. A colourless liquid was collected and this was freed from dissolved hydrogen sulphide by distilling it repeatedly over some more of the lead salt. The distillate (b.p. 100-120°), thus obtained, had the characteristic odour of acetic acid and it had no reducing properties. The silver salt was prepared and from this the silver content was found to be 64·59% corresponding exactly to that of silver acetate.

The bulk of the liquid was carefully fractionated and the fraction boiling at 113·5° had the equivalent weight 60·64 and consisted of pure acetic acid (m.p. of the *p*-toluidide, 146°; m.p. of the *p*-phenylphenacyl ester, 111°.)

Thus the volatile acids were found to consist principally of acetic acid together with a small quantity of benzoic acid.

Unsaponifiable Matter.

From the unsaponifiable matter only a small quantity of a phytosterol (m.p. 136°) could be isolated. Its acetate melted at 119°. The main bulk of the unsaponifiable matter, after a number of crystallisations from acetone gave a white granular non-nitrogenous material melting at 61-61·5°. This was neutral in character and did not give any tests for the presence of either hydroxyl or carbonyl groups. Considerable difficulty was felt in obtaining concordant combustion values. On keeping it for several days it gradually resinified.

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C-Alkyl Resorcinols. Part II. Synthesis of Polyalkyl Resorcinols.

By R. C. Shah and P. R. Mehta.

Although monoalkyl resorcinols and their derivatives have been much studied, comparatively little work appears to have been done on polyalkyl resorcinols. 4 : 6-Dialkyl resorcinols were synthesised for study of their phenol coefficients by Klarmann (*J. Amer. Chem. Soc.*, 1926, **48**, 2358). The present work was undertaken with the object of synthesising typical polyalkyl resorcinols containing more than two alkyl groups, which might be valuable as antiseptics.

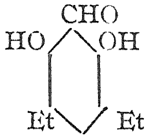
After this work was far advanced, Rosenmund, Buchwald and Deligiannis (*Arch. Pharm.*, 1933, **271**, 342) reported the synthesis of a number of 2:4:6-trialkylresorcinols, which were obtained by reduction of 4-alkyl-2:6-diacylresorcinols, produced from diacyl esters of 4-*n*-alkylresorcinols by the action of aluminium chloride in nitrobenzene solution.

In the present work, 4 : 6-diethyl-2-methyl-, 4-ethyl-5:6-dimethyl-, 4 : 6-diethyl-5-methyl-, and 4 : 6-diethyl-5 : 6-dimethyl-resorcinols have been synthesised, through the intermediate ketones and aldehydes. The *C*-alkyl resorcinol ketones obtained are of interest on account of their possible value as anthelmintics (*cf.* Karrer and Rosenfeld, *Helv. Chim. Acta*, 1921, **4**, 707). The *ortho*-hydroxy structure of the intermediate resorcylaldehydes was confirmed by (*i*) condensation with 5 : 6-dimethoxy-1-hydrindone by Perkin-Robinson method (*J. Chem. Soc.*, 1907, **91**, 1073), when characteristic pyrylium chlorides were obtained and (*ii*) by condensation with malonic or acetoacetic esters in the presence of piperidine by the Knoevenagel method (*Ber.*, 1904, **37**, 4461) which gave 3-carbethoxy- or 3-acetylalkyl coumarins.

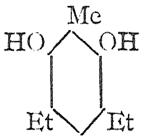
The various polyalkyl resorcinols are in general unstable crystalline substances and gradually decompose on standing. They give a bluish colouration with aqueous ferric chloride which rapidly fades away, probably due to oxidation. They are characterised by their high melting *p*-nitrobenzoyl derivatives, and further, those with their *o*-positions to the hydroxyl group free, were converted into alkyl coumarins by Pechmann condensation with acetoacetic ester and malic acid.

Synthesis of 4 : 6-*Diethyl*-2-*methylresorcinol.*

4 : 6-Diethylresorcinol was prepared according to Weiss and Kratz (*Monatsch.*, 1929, **51**, 386) and various reactions studied (*cf.* Part I, *Bombay University Journal*, 1935, p. 209). Although it did not undergo the Höesch reaction with acetonitrile, it was readily converted by the Gattermann reaction into 2 : 6-dihydroxy-3 : 5-diethylbenzaldehyde (I), a γ-resorcyl aldehyde. The bright yellow colour of the aldehyde may be explained by its existence in the tautomeric quinonoid form (*cf.* Robertson and Robinson, *J. Chem. Soc.*, 1927, 2196). Reduction of the aldehyde (I) by zinc amalgam prepared by the improved method of Robinson and Shah (*J. Chem. Soc.*, 1934, 1491) gave the required 4 : 6-diethyl-2-methylresorcinol (II).



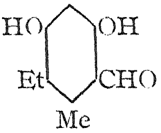
(I)



(II)

Synthesis of 4-*Ethyl*-5 : 6-*dimethylresorcinol.*

4-Ethyl-5-methylresorcinol (Robinson and Shah, *loc. cit.*), the reduction product of orsacetophenone, gave by the Gattermann reaction the aldehyde, whose probable constitution is that of a β-resorcylaldehyde viz., 6-methyl-5-ethyl-2 : 4-dihydroxybenzaldehyde (III), and not that of γ-resorcylaldehyde viz., 2 : 6-dihydroxy-4-methyl-5-ethyl-benzaldehyde. The β-resorcylaldehyde structure is supported by (*i*) analogy with known cases of Gattermann reaction on resorcinol derivatives, in which the aldehyde group usually enters the β-position which is much more accessible; and (*ii*) by the properties of the 3-carbethoxycoumarin resulting from the Knoevenagel condensation of the aldehyde with malonic ester, the coumarin derivative in solution in concentrated sulphuric acid or in dilute alkali showing strong fluorescence, characteristic of a 7-hydroxycoumarin, which can only result from a β-resorcylaldehyde (*cf.* Collie and Chrystall, *J. Chem. Soc.*, 1907, 1804; Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 407; Dey, *J. Chem. Soc.*, 1915, **107**, 1614, 1621). The aldehyde gave with 5 : 6-dimethoxy-1-hydrindone the characteristic pyrylium chloride. The Knoevenagel condensation with acetoacetic ester, however, produced abnormally a crystalline pyrylium salt with a green metallic reflex, instead of the expected 3-acetylcoumarin derivative. The pyrylium salt dissolved in alcohol with a permanganate colour, which turned deep blue on adding alkali. The formation of the pyrylium salt must be due to the further condensation of the 3-acetylcoumarin derivative, initially formed, with a second molecule of the hydroxy aldehyde to give the chalkone, which with hydrochloric acid would form the pyrylium salt. An analogous compound has only recently been obtained by Le Fèvere (*J. Chem. Soc.*, 1934, 450) from salicylaldehyde and acetoacetic ester in ethereal perchloric acid with hydrogen chloride as condensing agent. This interesting reaction will be more closely studied. Reduction of the aldehyde in the usual way led to the phenol of probable constitution, 4-ethyl-5 : 6-dimethyl resorcinol (IV).



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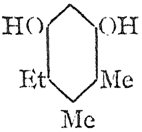

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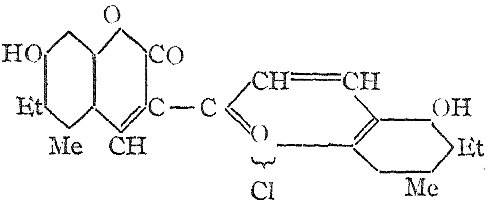
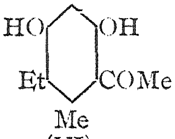


(V)

Synthesis of 4:6-Diethyl-5-methylresorcinol.

4-Ethyl-5-methylresorcinol by the Höesch reaction afforded the ketone whose probable constitution is 5-ethyl-6-methyl-2:4-dihydroxyacetophenone (VI). The ketone has been assigned the constitution (VI) of a β-acetylresorcinol derivative on the following grounds :— (*i*) Analogy with other cases of Höesch reaction on resorcinol compounds, (*ii*) the acetyl group cannot be introduced in the γ-position in the resorcinol nucleus by the Höesch reaction, as shown by the observation that 4:6-diethylresorcinol does not undergo the Höesch reaction, (*iii*) the diethylmethylresorcinol (VII) produced by the Clemmensen reduction of the ketone, when condensed with acetoacetic ester and malic acid give coumarins, which do not show fluorescence and are, therefore, 5-hydroxycoumarins, which can only result from a β-acetylresorcinol compound. If the ketone was a γ-acetylresorcinol derivative, the coumarins obtained would be 7-hydroxycoumarins.

Clemmensen reduction of the ketone yielded the phenol of the probable constitution 4:6-diethyl-5-methylresorcinol (VII).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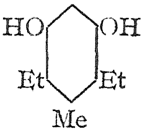
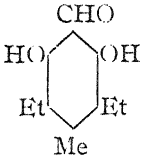

(VII)

Synthesis of 4:6-*Diethyl*-2:5-*dimethylresorcinol.*

3:5-Diethyl-4-methyl-2:6-dihydroxybenzaldehyde (VIII) was obtained from 4:6-diethyl-5-methylresorcinol (VII) in the usual manner. Its deep yellow colour may be explained similarly to (I). Reduction in aqueous alcoholic solution under properly regulated condition gave an excellent yield of 4:6-diethyl-2:5-dimethylresorcinol, the first tetra-alkylresorcinol (IX) to be synthesised.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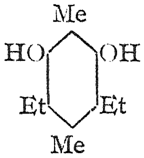
(IX)

The facile reduction by the Clemmensen method of 3:5-diethyl-2:6-dihydroxybenzaldehyde is remarkable, in view of the fact that 2:4-diacetyl- and 2:4-dipropionylresorcinols yield by Clemmensen reduction 4-ethyl- and 4-propylresorcinols, the acetyl-group in position 2 being split off (Rosenmund *et al, loc. cit.*).

EXPERIMENTAL.

3:5-*Diethyl*-2:6-*dihydroxybenzaldehyde* (I) was prepared by the Adams and Levene's modification of the Gattermann reaction (*J. Amer. Chem. Soc.*, 1923, **45**, 2373). To 4:6-diethylresorcinol (7 g.) dissolved in dry ether (150 c.c.) zinc cyanide (9·3 g.) was added, the mechanical stirrer started and dry hydrogen chloride gas passed in rapidly. After 1 hour, the ketimide hydrochloride began to separate as an oil, after which hydrogen chloride was passed for another hour. Ether was decanted off and the oily residue was washed with dry ether. Water (100 c.c.) was then added and the mixture heated at 100° for 1 hour. The oil which separated on cooling was extracted with ether. The residue from the ether extract which distilled as a yellow oil at 142-144°/2 mm. gradually solidified on cooling giving deep yellow flat needles, m.p. 68-70°. (Found: C, 68·0; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·1; H, 7·2 per cent). It decomposes gradually on standing, the solid becoming pasty and ultimately oily after few days. It gave a deep violet colouration with alcoholic ferric chloride. The p-*nitrophenylhydrazone* crystallised from dilute acetic acid in long chocolate coloured needles melting at 217-19°. (Found: N, 12·7. $C_{17}H_{19}O_4N_3$ requires N, 12·8 per cent).

Ethyl 6:8-*diethyl*-5-*hydroxycoumarin*-3-*carboxylate*.—Ethyl malonate (0·8 g.) was added to the aldehyde (I, 1 g.), 5 drops of piperidine were added at 0° and the reaction mixture was left for 2 days at room temperature. The dark yellow paste on treatment with dilute hydrochloric acid gave yellowish needles which crystallised from benzene in yellow needles, m.p. 155-57°. (Found**: C, 66·1; H, 6·3. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2 per cent). It did not show fluorescence in concentrated sulphuric acid solution or in alkaline solution.

6:8-*Diethyl*-5-*hydroxy*-5′:6′-*dimethoxy*-2:3(3′:2′)-*indenobenzopyrylium Chloride*.—Dry hydrogen chloride gas was passed for 2 hours into a solution of the aldehyde (I, 1g.) and 5:6-dimethoxy-1-hydrindone (1 g.) in dry ethyl acetate (5 c.c.). The deep orange leaflets obtained were washed several times with dry ether and dried, m.p. 209-10°. (Found: Cl, 9·4. $C_{22}H_{23}O_4Cl$ reqquires Cl, 9·2 per cent). The salt is easily hydrolysed, as the deep red aqueous acidic solution gradually decolourised and a yellowish precipitate, probably the related chalkone, ultimately separated. The *perchlorate* separated in deep red tiny needles on the addition of perchloric acid (5 c.c.). It was filtered, washed with dry methyl alcohol and dried, m.p. 155-58°. (Found: Cl, 7·9. $C_{22}H_{23}O_8Cl$ requires Cl, 7·9 per cent).

4:6-*Diethyl*-2-*methylresorcinol* (I).—To 30 g. of zinc amalgam, prepared from zinc dust according to Robinson and Shah (*loc. cit.*), the aldehyde (I, 7 g.) was added, followed by 50 c.c. of dilute hydrochloric acid (1:2) and the mixture heated at 100°. After 1 hour, 10 c.c. of concentrated HCl were added and the heating was continued for another hour. The solution was decanted off, saturated with common salt and extracted with ether. The unreacted zinc amalgam was also extracted with ether. The residue from the combined ether extract distilled as a colourless viscous oil at 170°/12 mm., and solidified on cooling in colourless plates, yield 4 g., m.p. 51-53°.

(Found : C, 73·0; H, 8·5. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9 per cent). It gave a transient blue colouration with aqueous ferric chloride.

The *di*-p-*nitrobenzoyl* derivative separated in long needles on shaking together an ethereal solution of *p*-nitrobenzoyl chloride and sodium hydroxide solution of (II). It crystallised from acetone-ethyl alcohol in colourless needles, m.p. 161-62°. (Found : N, 6·2. $C_{25}H_{22}O_8N_2$ requires N, 5·9 per cent).

Dibenzoyl derivative of Orsacetophenone.—A mixture of orsacetophenone (2 g.), benzoyl chloride (5 c.c.) and pyridine (12 c.c.) was left at room temperature for 12 hours, acidified with dilute sulphuric acid and extracted wtih ether. The oily residue from the ethereal extract solidified after several days and crystallised from dilute alcohol in greyish shining plates, m.p. 97-98°, yield 0·6g. (Found : C, 73·4; H, 4·7. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·8 per cent).

Di-p-*nitrobenzoyl Derivative of 4-Ethyl-5-methylresorcinol* crystallised from acetone-ethyl alcohol in colourless needles, m.p. 173°-174°. (Found: N, 6·5. $C_{23}H_{18}O_8N_2$ requires N, 6·2 per cent). It is insoluble in the usual organic solvents except acetone.

4-*Ethyl*-5-*methyl*-6-*acetoxy*-*mercuri*-*resorcinol*. —4-Ethyl-5-methylresorcinol (1 g.) in alcoholic solution was added to a suspension of mercuric acetate (2 g.) in the same solvent. The yellow product crystallised from boiling acetic acid in tiny orange needles which blackened at 200° and did not melt up to 315°, yield 2·1 g. (Found: Hg, 48·5. $C_{11}H_{14}O_4$ Hg requires Hg, 48·9 per cent)·

5-*Methyl 6-ethyl-7-hydroxycoumarin*.—Concentrated sulphuric acid (85%; 15 c.c.) was slowly added to a mixture of 4-ethyl-5-methylresorcinol (1·5 g.) and malic acid (1·3 g.), and after 12 hours was heated at 100° for 1 hour, cooled and poured into ice-cold water. The precipitate crystallised from dilute alcohol in greyish needles, m.p. 211-12°, yield 1 g. (Found*: C, 70·4; H, 5·6. $C_{12}H_{13}O_3$ requires C, 70·6; H, 5·9 per cent). It gave a light blue fluorescence in concentrated sulphuric acid and in alkaline solution and hence it is formulated as a 7-hydroxy coumarin. (*cf.* Collie and Chrystall, *loc. cit.*; Chakravarti, *loc. cit.*; Dey, *loc. cit.*)

4:7-*Dimethyl*-6-*ethyl*-5-*hydroxycoumarin*.—A mixture of concentrated sulphuric acid (85% ; 10 c.c.), 4-ethyl-5-methyl resorcinol (1·5 g.) and ethyl acetoacetate (1·3 g.) was kept at room temperature for 1 hour, heated at 100°, cooled and poured into ice-cold water. The dirty pasty mass solidified after 2 hours and crystallised from dilute alcohol in colourless flat needles, m.p. 187-89°, yield 1·3 g. (Found*: C. 71·3; H, 6·5. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4 per cent). It is regarded as a 5-hydroxy compound as it does not show light blue fluorescence in sulphuric acid and in alkaline solution.

2-*Methyl*-3-*ethyl*-4:6-*dihydroxybenzaldehyde* (III) was prepared similarly to (I) from 4-ethyl-5-methylresorcinol (8·5 g.) dissolved in dry ether (120 c.c.) and zinc cyanide (14 g.). Hydrogen chloride gas was passed for 2½ hours, after which the separated oily ketimide hydrochloride was heated with water (200 c.c.) at 100° for 1½ hours. The solid, which separated on cooling, crystallised from dilute ethyl alcohol in yellow needles, m. p. 161-62°, yield 5·1 g. (Found:* C, 66·8; H, 6·8. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7 per cent). It gave a dark violet colouration with alcoholic ferric chloride. The p-*nitrophenylhydrazone* crystallised from dilute alcohol in orange wooly needles, m.p. 255°-257°. (Found: N, 13·1. $C_{16}H_{17}O_4N_3$ requires N, 13·3 per cent).

Ethyl 5-*methyl*-6-*ethyl*-7-*hydroxycoumarin*-3-*carboxylate* was prepared from the foregoing aldehyde (III, I g.), malonic ester (0·9 g.) and 4 drops of piperidine. It crystallised from benzene in yellowish thick plates, m. p. 165-67°, yield 1 g. (Found: C, 65·2; H, 6·2. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8 per cent). It dissolved in concentrated sulphuric acid giving a beautiful green fluorescence. Its alkaline solution also showed similar fluorescence.

Condensation of 2-*Methyl*-3-*ethyl*-4:6-*dihydroxybenzaldehyde with ethyl acetoacetate.*—To a mixture of the aldehyde (III, 1 g.) and ethyl acetoacetate (0·9 g.) piperidine (4 drops) was added at 0° and the mixture kept at room temperature for 5 hours. The pasty mass on treatment with dilute hydrochloric acid gave a dark red solid which crystallised from a mixture of acetic acid and dilute hydrochloric acid in brilliant needle-shaped crystals with a green metallic reflex, m.p. 295-98°. (Found : Cl, 8·1. $C_{24}H_{25}O_5Cl$ requires Cl, 8·3 per cent). The pyrylium salt (V) when dissolved in ethyl alcohol gave a permanganate colour, which changed to deep blue on addition of alkali, the blue colour base being formed. It gave a bluish green fluorescence with concentrated sulphuric acid.

5-*Methyl*-6-*ethyl*-7-*hydroxy*-5':6'-*dimethoxy*-2:3 (3':2')-*indenobenzopyrylium Chloride.*—Dry hydrochloric acid gas was passed at 0° for 2 hours into a mixture of the aldehyde (III, 1 g.) and 5:6-dimethoxy-1-hydrindone (1 g.) dissolved in the minimum quantity of ethyl acetate. The shining red plates darkened above 300°. (Found: Cl, 9·5. $C_{21}H_{21}O_4Cl$ requires Cl, 9·5 per cent). An aqueous acidic solution gradually decolourised and a yellowish precipitate ultimately separated out. The *perchlorate* prepared by adding perchloric acid to a methyl alcoholic solution of the pyrylium chloride separated in orange needles. It darkened at 260° and did not melt up to 315°. (Found: Cl, 8·2. $C_{21}H_{21}O_8Cl$ requires Cl, 8·1 per cent).

4-*Ethyl*-5:6-*dimethylresorcinol* (IV).—A mixture of zinc amalgam (from 10 g. of zinc dust), the aldehyde (III, 2·3 g.) and 30 c.c. of dilute hydrochloric acid (1:1) was heated at 100° for 1 hour, when the feebly acidic solution gave no colouration with ferric chloride. The decanted solution deposited colourless crystals, which crystallised from hot alcohol in colourless flat needles, m.p. 145-46°, yield 1·4 g. (Found*: C, 72·4; H, 8·3. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4 per cent). It gave a greenish blue colouration with aqueous alcoholic ferric chloride. The phenol turned brown on keeping for a month and the melting point was then 120-130°. The *di*-p-*nitrobenzoyl* derivative crystallised from acetone-ethyl alcohol in tiny colourless needles, m.p. 224-25°. (Found: N, 6·0. $C_{24}H_{20}O_8N_2$ requires N, 6·0 per cent).

5-*Ethyl*-6-*methyl*-2:4-*dihydroxyacetophenone* (VI).—Dry hydrogen chloride gas was passed at 0° for 3 hours into a mixture of 4-ethyl-5-methylresocinol (20 g.), acetonitrile (14 g.), dry ether (130 c.c.) and powdered fused zinc chloride (9·2 g.). The dark red oil which separated, solidified on keeping for 12 hours at 0°. It was washed with dry ether and treated with crushed ice. The yellowish crystalline substance was crystallised from boiling acetic acid in yellow plates, m.p. 237-38°, yield 11 g. (Found: Cl, 15·2. $C_{11}H_{16}O_2NCl$ requires Cl, 15·5 per cent). The hydrolysis of the ketimide hydrochloride was effected by boiling with water for 1½ hours. On cooling dirty brown small plates separated which were collected and crystallised from benzene-petroleum ether in brownish shining plates, m.p. 107-108°, yield 9 g. (Found* : C, 68·2 ; H, 7·4. $C_{11}H_{14}O_3$ requires C, 68·1 ; H, 7·2 per cent). It gave a dark violet colouration with alcoholic ferric chloride. The *dibenzoyl* derivative, which was prepared similarly to that of orsacetophenone, crystallised from dilute alcohol in shining flat needles, m.p. 61-63°, yield 0·26 g. (Found : C, 74·2 ; H, 5·6. $C_{25}C_{22}O_5$ requires C, 74·4 ; H, 5·5 per cent). It is insoluble in alkali and does not give any colouration with alcoholic ferric chloride. The *phenylhydrazone* crystallised from dilute alcohol in yellow needles, m.p. 197-98°. (Found : N, 9·6. $C_{17}H_{21}O_2N_2$ requires N, 9·8 per cent).

4 : 6-*Diethyl*-5-*methylresorcinol* (VII).—A mixture of zinc amalgam (from 80 g. zinc dust), the foregoing ketone (VI, 20 g.) and dilute hydrochloric acid (1 : 1, 70 c.c.) was heated at 100°. When the

reaction moderated down, more dilute hydrochloric acid (60 c.c.) was added. Reduction required 2 hours. The product separating on cooling crystallised from hot water in flat colourless needles, m.p. 80°, yield 12 g. (Found*: C, 73·4; H, 9·0. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0 per cent). It gave a transient blue colouration with aqueous ferric chloride. The *di*-p-*nitrobenzoyl* derivative crystallised from boiling acetic acid in colourless shining needles, m. p. 243-45°. (Found: N, 6·0. $C_{25}H_{22}O_8N_2$ requires N, 5·9 per cent).

Diacetyl Derivative.—A mixture of the phenol (VIII, 2·3 g.), acetic anhydride (10 c.c.) and pyridine (5 drops) was kept for 1/2 hour, refluxed for 1 hour and poured into water. It was crystallised from dilute alcohol in shining buttons, m.p. 69-70°, yield 1·7 g. (Found*: C, 68·1; H, 7·2. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6 per cent).

6 : 8-*Diethyl-7-methyl-5-hydroxycoumarin*, prepared similarly to 5-methyl-6-ethyl-7-hydroxycoumarin, crystallised from dilute alcohol in shining needles, m.p. 183-85°, yield 0·5 g. (Found*: C, 72·2; H, 6·8. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9 per cent). It did not show fluorescence in concentrated sulphuric acid or in alkali solution.

6 : 8-*Diethyl-4 : 7-dimethyl-5-hydroxycoumarin*, prepared by the method described for 4 : 5-dimethyl-6-ethyl-7-hydroxycoumarin, crystallised from dilute alcohol in brown needles, m. p. 179-80°, yield 0·5 g. (Found*: C, 72·9; H, 7·0. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3 per cent). It did not show fluorescence in sulphuric acid or alkaline solutions.

3 : 5-*Diethyl-4-methyl-2 : 6-dihydroxybenzaldehyde* (VIII) was prepared as usual from 4 : 6-diethyl-5-methylresorcinol (VII, 3 g.) dissolved in dry ether (110 c.c.) and zinc cyanide (4·2 g.). The dry hydrogen chloride gas was passed for 1½ hours. The crystalline ketimide hydrochloride was heated with water (200 c.c.) at 100° for 1 hour. The product crystallised from light petroleum ether (b.p. 69-95°) in flat shining yellow needles, m.p. 117-18°, yield 2 g. (Found*: C, 69·4; H, 7·9. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7 per cent). The p-*nitrophenylhydrazone* crystallised from hot acetic acid in deep red shining needles, m. p. 224-25°. (Found: N, 12·3. $C_{18}H_{21}O_4N_3$ requires N, 12·3 per cent).

Ethyl 6 : 8-*diethyl-7-methyl-5-hydroxycoumarin-3-carboxylate* from the aldehyde (VIII, 0·7 g.), malonic ester (0·54 g.) and piperidine (3 drops) crystallised from dilute alcohol in yellow wooly needles, m.p. 181-83°, yield 0·51 g. (Found: C, 67·1; H, 6·7. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·7 per cent). It showed no fluorescence in concentrated sulphuric acid or in alkali solution.

6 : 8-*Diethyl-7-methyl-5-hydroxy-5′ : 6′-dimethoxy-2 : 3 (3′ : 2′) indenobenzopyrylium Chloride.*—Dry hydrogen chloride was passed for 2 hours into a mixture of the aldehyde (VIII, 0·8 g.) and 5 : 6-dimethoxy-1-hydrindone (0·71 g.) in dry ethyl acetate (5 c.c.). It was obtained in dark red needles which melted at 153°-54°. (Found : Cl, 8·8. $C_{23}H_{25}O_4Cl$ requires Cl, 8·9 per cent). The *perchlorate* melted at 240°-241°. (Found : Cl, 7·9. $C_{23}H_{25}O_8Cl$ requires Cl, 7·6 per cent).

4 : 6-*Diethyl-2 : 5-dimethyl resorcinol* (IX).—A mixture of zinc amalgam (from 10 g. of zinc dust), 20 c.c. of dilute (1 : 1) hydrochloric acid and the aldehyde (VIII, 2 g.) dissolved in ethyl alcohol was gradually heated at 100° until the yellow colour of the mixture was discharged (30 minutes). Longer heating is undesirable. The hot solution, after filtration, deposited on cooling a white spongy mass which crystallised from dilute alcohol in colourless needles, m.p. 107°-108°. (Found : C, 74·6 ; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2 ; H, 9·3 per cent). It gave a blue colouration with aqueous ferric chloride which disappeared after some time. It deteriorates rapidly on cooling, becoming deep brown even in a day and after two or three days becomes pasty. The *di-*p-*nitrobenzoyl* derivative crystallised from boiling acetic acid in tiny white needles, m.p. 257-59°, yield 1·7 g. (Found : N, 5·8. $C_{25}H_{21}O_8N_2$ requires N, 5·7 per cent).

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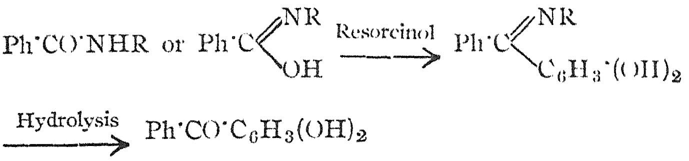
The analysis marked** is a micro-analysis, carried out by Dr. J. N. Ray of Lahore ; those marked * are micro-analyses carried out by Dr. Fischer of Germany and the remaining were done by one of the authors (P. R. M.).

A New and Convenient Synthesis of 2:4-Dihydroxybenzophenone

BY R. C. SHAH and P. R. MEHTA.

It has been known that dialkylaminobenzophenones can be prepared by the condensation of benzanilides with dialkylanilines in the presence of phosphorus oxychloride (D.R.P. 41751; Friedlander, **I**, 44,47; Meisenheimer, Budkewicz and Kananow, *Annalen*, 1921, **423**, 75; Shah, Deshpande and Chaubal, *J. Chem. Soc.*, 1932, 642). The authors attempted a similar condensation under various conditions, using resorcinol in place of a dialkylaniline, but no condensation took place and benzanilide was more or less completely recovered unchanged. However, with a mixture of fused zinc chloride and phosphorus oxychloride as a condensing agent, the expected condensation readily took place with a 30% yield of 2:4-dihydroxybenzophenone, though zinc chloride alone was ineffective. The condensation proceeded still better when benzanilide was replaced by benzamide, the yield being 35%. The probable course of the reaction is as follows, the intermediate product being a ketimide as in the Höesch synthesis:



$$\mathrm{Ph\cdot CO\cdot NHR} \text{ or } \mathrm{Ph\cdot C}\begin{matrix} /\!\!/\mathrm{NR} \\ \backslash\mathrm{OH} \end{matrix} \xrightarrow{\text{Resorcinol}} \mathrm{Ph\cdot C}\begin{matrix} /\!\!/\mathrm{NR} \\ \backslash\mathrm{C_6H_3\cdot(OH)_2} \end{matrix}$$

$$\xrightarrow{\text{Hydrolysis}} \mathrm{Ph\cdot CO\cdot C_6H_3(OH)_2}$$

(R = Ph in the case of benzanilide; R = H in the case of benzamide).

In the experiment with benzamide, a neutral oil was also obtained and this was identified as benzonitrile, which must have been formed by the dehydrating action of phosphorus oxychloride on a part of the benzamide. A mixture of benzamide and phosphorus oxychloride at 100° gave an almost quantitative yield of benzonitrile. This observation was extended to some other amides also, but as we have been anticipated in this respect by Von Braun and Rudolph (*Ber.*, 1934, **67**, 1762), who have made a similar observation, an account of these experiments is not included.

As a matter of independent interest, several other possible methods for the preparation of 2:4-dihydroxybenzophenone were also investigated.

The known method in which benzoic acid is heated with resorcinol in the presence of zinc chloride (Komarowsky and Kostanecki, *Ber.*, 1894, **27**, 1997) is of no preparative value, as the yield was only 2·1 g. from 20 g. of resorcinol. Attempted condensation of benzoic acid and resorcinol with concentrated sulphuric acid or phosphorus oxychloride was unsuccessful. Condensation with the help of stannic chloride gave in one experiment a 49% yield, but the experiment could not be repeated and subsequent experiments gave very low yields. Condensation in benzene with phosphoric anhydride gave resorcinol monobenzoate, resorcinol dibenzoate and 2:4-dihydroxybenzophenone (poor yield). Benzanilide did not condense with resorcinol in the presence of phosphoric anhydride.

EXPERIMENTAL.

A mixture of benzanilide (10 g.), resorcinol (6 g.) and phosphorus oxychloride (20 c.c.) was heated in various experiments at temperatures ranging from 120° to 170° for 1 hour. The pasty mass was treated with ice-cold water, and the insoluble residue was boiled with 2*N*-NaOH for 1/2 hour. The filtered alkaline solution yielded nothing on acidification, and the product insoluble in alkali was found to be benzanilide (8-9 g.).

Condensation of Benzanilide with Resorcinol.—Benzanilide (10 g.) and resorcinol (6 g.) were mixed together and freshly fused powdered zinc chloride (10·5 g.) added, followed by phosphorus oxychloride (20 c.c.). The mixture was heated in an oil-bath at 130°-140°, until hydrogen chloride ceased to be evolved (1 hr.). After cooling, ice-water was added, and the insoluble residue boiled with excess of 2*N*-NaOH for 1/2 hour and filtered to remove unchanged benzanilide. Acidification of the filtrate gave a dirty greyish semisolid mass, which crystallised from much hot water in greyish needles, m.p. and mixed m.p. with an authentic specimen of 2 : 4-dihydroxybenzophenone prepared from resorcinol by the

Höesch reaction, m.p. 144-45°, yield 3 g. It dissolved in dilute alkali and gave a dark violet colouration with alcoholic ferric chloride. The identity was further confirmed by the preparation of the dibenzoyl derivative, m.p. 140-41°; Döbner (*Annalen*, 1881, **210**, 258) gives m.p. 141°.

Condensation of Benzamide with Resorcinol.—A mixture of benzamide (10 g.), resorcinol (9 g.), fused zinc chloride (11·2 g.) and phosphorus oxychloride (20 c.c.) was heated in an oil-bath. At about 100° the evolution of hydrogen chloride began. The temperature was gradually raised to 140° in the course of one hour by which time the evolution of hydrogen chloride became negligible. Water was added to the cooled melt and the mixture was heated at 100° and filtered hot to remove unreacted benzamide. The insoluble semicrystalline mass was boiled with 2*N*-NaOH for ½ hour. After cooling, the oil which had separated was extracted with ether. The residue from the ether extract was a colourless oil, b.p. 187-89°, and was identified as benzonitrile. The alkaline solution on acidification with concentrated HCl, deposited brownish needles of 2 : 4-dihydroxybenzophenone, which crystallised from hot water in colourless needles, m.p. 144-45°. A mixed m.p. with the product obtained from the previous experiment and with an authentic specimen showed no depression, yield 3·5—4·0 g.

Condensation of Benzoic Acid and Resorcinol.—(*i*) The mixture of resorcinol (20 g.), zinc chloride (30 g.) and benzoic acid (30 g.) was heated at 160° for 13 minutes. The cooled melt was washed with cold water and then with saturated $NaHCO_3$ solution. The residue on crystallisation from hot water gave colourless needles of 2 : 4-dihydroxybenzophenone (2·1 g.).

(*ii*) *With stannic chloride.*—Benzoic acid (30 g.) and anhydrous stannic chloride (30 g.) were heated together until a homogeneous liquid was formed. Resorcinol (20 g.) was then added and the mixture heated at 140-150° for ½ hour. The mixture when cold was washed successively with water, concentrated hydrochloric acid and saturated $NaHCO_3$ solution. The residue on crystallisation from hot water melted at 119-130° and was found to be a mixture of two substances. Separation was effected by hot petroleum ether (b.p. 65-95°), which on cooling deposited colourless prismatic needles (m.p. 113°), probably monobenzoyl derivative of 2 : 4-dihydroxybenzophenone. (Found : C, 75·1; H, 4·7. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4 per cent). The compound insoluble in petroleum ether was found to be 2 : 4-dihydroxybenzophenone. A further quantity of the ketone was obtained from the compound, m.p. 113°, by boiling in NaOH solution for ¼ hour and subsequent acidification with concentrated HCl. The total yield of the ketone was 12·0 g. in one experiment but the experiment could not be repeated, yields in subsequent experiments being yery poor.

(*iii*) *With phosphoric anhydride.*—Benzoic acid (20 g.), resorcinol (24 g.) and phosphoric anhydride (25 g.) in benzene (80 c.c.) were heated together in an oil-bath (120°-130°) for 15 minutes. The benzene layer was washed with saturated $NaHCO_3$ solution and then extracted with sodium hydroxide solution. The alkaline extract on acidification gave a solid, which on crystallisation from alcohol melted at 136°, and was proved to be resorcinol monobenzoate by direct comparison with an authentic specimen. The residue from benzene layer was a solid which melted at 119°, after crystallisation from alcohol and was found to be resorcinol dibenzoate. The solid remaining after decanting off the benzene solution was treated with ice and then with saturated $NaHCO_3$ solution. The insoluble residue crystallised from hot water in needles, m p. 144-45°, and was found to be 2 : 4-dihydroxybenzophenone. The yield was poor.

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Variation of the Cataphoretic Velocity of Colloidal Particles during Aggregation. Part I.

By Jnanendra Nath Mukherjee, Subodh Gobinda Chaudhury and Krishnadhan Bhabak.

The cataphoretic velocity of colloidal particles often shows a minimum, followed by a continuous increase as the concentration of a uni-univalent electrolyte added to a colloidal solution increases (Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, **2**, 296; Mukherjee, Chaudhury and Roychaudhury, *ibid.*, 1927, **4**, 493; Mukherjee, Roychoudhury and their co-workers, *ibid.*, 1928, **5**, 697, 735). Near about the stage of appearance of visible aggregates and the breaking up of the colloidal solution into a precipitated mass, a sudden fall of the cataphoretic velocity takes place (Mukherjee, Chaudhury and Roychoudhury, *loc. cit.*). It has been suggested (Mukherjee *et al*, *loc. cit.*, *cf.* also Mukherjee, Chaudhury and Ghosh, *Trans. National Inst. Sci. India*, 1935, **1**, 47), that the increase in the cataphoretic speed near about coagulating concentrations is a direct consequence of the aggregation of the colloidal particles. It was also suggested that even at the high concentrations of uni-univalent electrolytes, which are used, the primary adsorption of similarly charged ions is not likely to be so preponderant over the electrical adsorption of oppositely charged ions, as to increase the cataphoretic velocity to the extent which has been actually observed.

These observations and suggestions have an important bearing on the theories of cataphoresis and of the electrical double layer. In recent years, the dependence of the cataphoretic velocity on the size and shape of a colloidal particle has been investigated both theoretically and experimentally by Freundlich and Abramsohn (*Z. physikal. Chem.*, 1927, **128**, 25; 1928, **133**, 51), Abramsohn, (*J. Gen. Physiol.*, 1929, **12**, 711; *J. Phys. Chem.*, 1931, **35**, 291) and Mooney (*Phys. Rev.*, 1924, **23**, 396; 1931, **35**, 331), Henry, (*Proc. Roy. Soc.*, 1931, **A**, **133**, 106) and Bikermann (*Z. physikal. Chem.*, 1934, **A**, **171**, 209).

The Debye and Hückel theory of strong electrolytes which is valid for very low ionic strengths, has in recent years often been drawn upon to formulate the dependence of the cataphoretic velocity on the ionic strength of the colloidal solution (*cf.* Abramsohn, *loc. cit.*, Henry, *loc. cit.*).

In discussions on the above subjects, three aspects are generally ignored, these are (*a*) the interionic repulsions between the mobile ions in the double layer to which is to be attributed the stabilising influence of the electrical charge of the particle, (*b*) the effect of the aggregation on the distribution of ions in the double layer, (*c*) the special rôle of the adsorption of ions, and (*d*) the contribution of the colloidal particles to the ionic strength of the medium, an estimate of which involves a knowledge of the number and valency of the colloidal ions and of the mobile ions associated with them. These aspects also raise the more general question as to how far the Debye-Hückel concepts are valid for the peculiar distribution of electrical charges round colloidal particles (Mukherjee, *Kolloid Z.*, 1933, **62**, 257; 1933, **63**, 36; 1933, **65**, 71; 1934, **67**, 178). Investigations on the effect of the aggregation of colloidal particles on the cataphoretic velocity under conditions where the ionic strength may be assumed to be constant as a first approximation afford valuable information likely to throw considerable light on the whole subject. It will be seen from the sequel that concurrent with the process of aggregation in the region of slow coagulation, the cataphoretic velocity of the aggregates increases. There are also cases where a diminution has been observed and the sudden fall in the cataphoretic velocity near the stage of the precipitation of the colloid has been confirmed. It has been shown in this paper that the theories which ignore the aspects mentioned above are inadequate, and the relationships between cataphoretic velocity and size and shape of particles suggested in recent years are not valid and that detailed considerations of the distribution of ions in the double layer and their adsorption are necessary.

EXPERIMENTAL.

The best course to follow the effect of aggregation on the c.v. experimentally is to add a definite concentration of an electrolyte to a colloid which coagulates a particular sol in a time sufficient to permit the measurement of the c.v. during the progress of aggregation. For this, the micro-cataphoretic apparatus is more suitable than the **U**-tube method, though the latter method gave sufficient indications that such an effect exists (*cf.* Mukherjee, Roychoudhury and Biswas, *J. Indian Chem. Soc.*, 1931, **8**, 373). The micro-cataphoretic apparatus with reversible electrodes used by us is essentially the same as that of Northrop (*J. Gen. Physiol.*, 1922, **4**, 629) as modified by Freundlich and Abramsohn (*loc. cit.*) with the further modification that the main cell can be detached from the electrode vessels. The rectangular cell is fitted with *detachable* three-way stop-cocks, at either ends, which permit of ease of cleansing the different parts.

The cataphoretic velocity in cm./sec. per volt/cm. is calculated from Smoluchowski's equation,

$$V=\tfrac{3}{4}V_{\frac{1}{6}}+\tfrac{1}{4}V_{\frac{1}{2}}$$

where $V_{\frac{1}{6}}$ and $V_{\frac{1}{2}}$ are the observed velocities of the particles at $\frac{1}{6}$ and $\frac{1}{2}$ height of the cell. Measurements of velocities at different heights of the cell show that the curve relating the velocity with different depths of the cell is approximately a parabola (*cf.* Fig. 1 and Table I), as required by theory. The numbers in the following tables give the c.v. multiplied by 10.^{5}

TABLE I.

Arsenious sulphide sol and potassium chloride.

Height	...	1/9	1/6	1/4	1/3	2/5	1/2	3/5	2/3
$V^* \times 10^5$	...	46·7	51·4	54·16	54·54	50·55	47·83	—	—

$$V=\tfrac{3}{4}\ V_{\frac{1}{6}}+\tfrac{1}{4}\ V_{\frac{1}{2}}=50{\cdot}51\times10^5.$$

Height	...	0·05	0·1	0·15	0·2	0·25	0·3	0·35	0·4	0·45	0·5
$V^* \times 10^5$	...	39·36	44·5	51·69	51·69	53·64	53·04	50·41	47·35	50·41	47·65

$$V=\tfrac{3}{4}\ V_{\frac{1}{6}}+\tfrac{1}{4}\ V_{\frac{1}{2}}=50{\cdot}68\times10^5$$

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* Velocity, V in cm/sec. per volt/cm.

The reproducibility of the results is illustrated by the figures in Table I, and is within 1% when sufficient care is taken to cleanse the cell properly and the current is kept constant within 0·1 of a milliamp. Results given in Table II were taken without the precautions, stated above and though they were not concordant, it will be seen that the effect of time on c. v. of As_2S_3 sol in presence of potassium chloride is definitely marked.

TABLE II.

Preliminary results with arsenious sulphide sol and potassium chloride (N/6).

* Time (counted since the colloid and electrolyte were mixed) during which the measurements were made.	$V \times 10^5$.		* Time (counted since the colloid and electrolyte were mixed) during which the measurements were made.	$V \times 10^5$.
7— 23 min.	35·81 cm./sec. per volt/cm.	23·5 †	5— 13 min.	49·58 cm./sec. per volt/cm.
35— 45	50·94	23·40 ‡	40— 51	55·33
55— 65	52·0		75— 83	56·18
85—115	52·5		4— 15	35·2
200—210	52·3		34— 90	38·66
220—230	50·7		120—135	42·24
5— 13	55·31		5— 25	42·85
39— 51	61·53		75— 87	49·41
72— 85	60·52			
95—110	60·17			

In Tables III to VI, the effect of time and aggregation on the c. v. of particles of arsenious sulphide, palmitic acid, vanadium pentoxide, and tungstic acid sols have been given. The above sols were polydisperse and were of different grades of dispersion. The arsenious sulphide sols referred to in Tables I, II, III, IV and V were finely dispersed and with the magnification used (eye-piece, 28X, objective 20 mm.), the particles of the pure sol could rarely be seen under the microscope. As, however, the coagulation proceeds, the aggregates become visible. From the number of divisions of the micrometer eye-piece, with which the linear dimensions of the aggregates coincide and from the magnification, the size of the aggregates has been calculated. It is often observed that on the application of the electric field, the particles became visible though practically none were observed in its absence. It appears that under these conditions, the number of particles of sufficiently large size was very small and with the application of the field, the resulting cataphoresis brings into the field of observation more particles. Besides, the motion helps the visual observation. The size of the particles varied from 3·1 μ downwards in the case of the pure sols, whereas in presence of electrolytes, the size varied from 3·1 μ to 15·5 μ.

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* In the above table the times given have the same significance.

† $V \times 10^5$ after coagulation.

‡ Velocity of the coagula thoroughly shaken with the supernatant liquid.

FIG. 1.

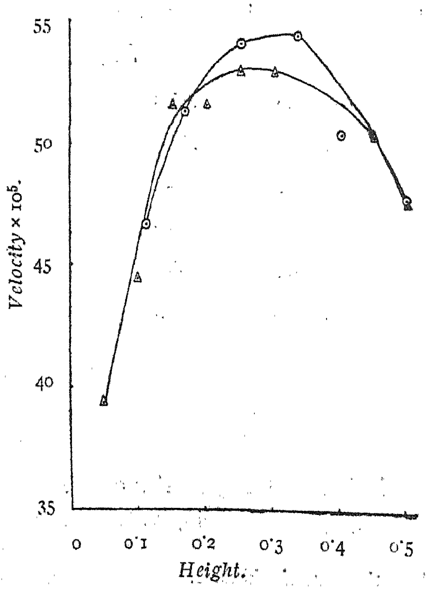
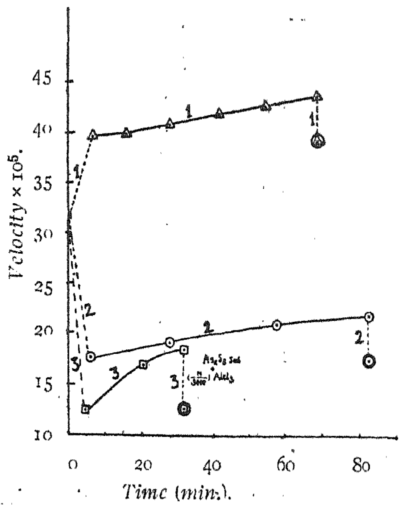


FIG. 2.
$AS_2 S_3$ *sol.*



Curves 1-3 refer respectively to $N/7$-KCl, $N/309$-$BaCl_2$ and $N/300$-$AlCl_3$.
○ means C. V. after coagulation.

The coagulating electrolytes were potassium chloride, barium chloride and aluminium chloride. The concentration of the electrolyte was so chosen that it took about 1-2 hours for coagulation to take place. Equal volumes of a sol and an electrolyte were taken in two beakers and mixed by pouring the electrolyte to the sol. The time of mixing was noted. Measurements were then taken during the process of coagulation at noted intervals of time. After a definite time for a particular concentration of electrolyte, the sol was seen to be partially coagulated. The supernatant solution was decanted off and the c. v. of the particles in it measured.

Arsenious Sulphide Sol.

The arsenious sulphide sol has been prepared as described before (Mukherjee and Chaudhury, *loc. cit.*). Measurements were also taken by shaking the coagula with the supernatant suspension of the colloid after coagulation. These results have been collected together in Tables III and IV and the curves have been shown in Fig. 2.

TABLE III.

Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
Water		27·24	45·00	31·65			
$N/9$-KCl	12-21 min.	36·56	51·95	40·42	31·1	47·56	35·2
	40-55	40·2	54·6	43·75			
	2-12	35·22	51·92	39·4			
	32-38	40·71	56·85	44·74			
	5-12	36·49	52·35	40·7			
	40-45	43·26	53·37	45·78			
	77-84	40·64	56·72	44·66	26·53	54·62	33·54
	6-10	34·81	52·94	39·34			
	46-50	39·89	56·16	43·95	32·91	45·71	36·08
	4-10	37·81	50·76	41·04	32·57	42·16	32·96
	36-44	39·75	58·43	44·39	33·7	48·76	36·4*

* Supernatant coagulated sol thoroughly shaken with the original precipitate and velocity measured.

TABLE III (contd.).

Electrolyte.	Time after mixing.	Before coagulation.			After centrifuging.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
N-KCl	10-18 min.	34·81	40·08	38·27			
	30-40	36·26	52·17	40·48			
	56-63	40·04	50·42	42·23			
	4-13	35·73	48·74	38·97	36·64	48·92	39·68
	68-74	38·98	55·2	43·02			
	5-11	35·47	48·83	39·78	36·72	49·74	39·95
	43-47	41·42	52·23	43·95			
	10-14	36·54	47·26	39·23			
	60-64	40·47	52·38	43·95	36·99	49·42	40·07
	5-8	36·41	49.04	39·56			
	13-18	36·53	49·66	39 8			
	25-30	37·78	50·32	40·9	36·4	49·2	39·6
	38-44	38·9	50·65	41·92			
	50-58	39·9	50·87	42·62			
	64-72	40·8	51 9	43·6			
	12-16	36·09	51·53	39·94			
	21-28	37·15	50·63	40·33			
	24 hrs.	47·66	59·16	49·77	44·49	56·4	47·67
	14-28	35·52	53·63	40·04			
	24 hrs.	46·65	60·15	50·01			

TABLE IV.

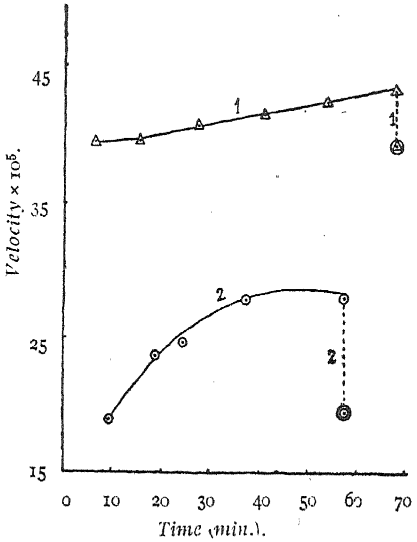
Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
N/300-$BaCl_2$	6-10 min.	16·5	20·1	17·11	16·15	21·8	17·54
	52-58	20·21	23·66	21·06			
	3-10	16·53	20·7	17·53			
	25 31	18·13	22·57	19·23	16·35	21·74	17·67
	55-60	20·6	23·14	21·23			
	80-85	21·19	24·44	21·98			
N/350-$BaCl_2$	10-15 min.	16·01	20·29	17·07			
	70-73	19·87	24·52	21·01	17·5	21·3	18·53
	3-13	16·43	20·65	17·46	17·3	21·59	18·6
	50-58	18·92	25·36	22·02			
N/400-$BaCl_2$	5-13	14·67	17·12	15·28	15.35	22·88	17·23
	115-120	18·26	25·36	20·03			
	5-15	13·36	16·01	14·02			
	85-95	18·8	26·91	20·85	15·39	23·03	17·27
N/2500-$AlCl_3$	8-13	16·42	23·89	18·28	12·4	16·56	13·46
	43-50	21·47	28·07	23·09			
	7-12	16·93	23·42	18·54	12·09	16·87	13·27
	44-49	21·76	29·67	23·73			
N/3000-$AlCl_3$	3-8	10·85	16·67	12·19			
	19-22	15·68	20·72	16·94	11·54	13·96	12·13
	30-34	17·06	22·78	18·47			

Palmitic Acid Sol.

Palmitic acid sol has been prepared as described below. 50 C.c. of a saturated solution of palmitic acid in alcohol were added slowly to 500 c.c. of warm water. It was kept overnight when some acid was coagulated and floated above. The clear sol was pipetted out for experiments. The sol became coarser after a few days. Table V and Fig. 3 illustrate the results.

FIG. 3.

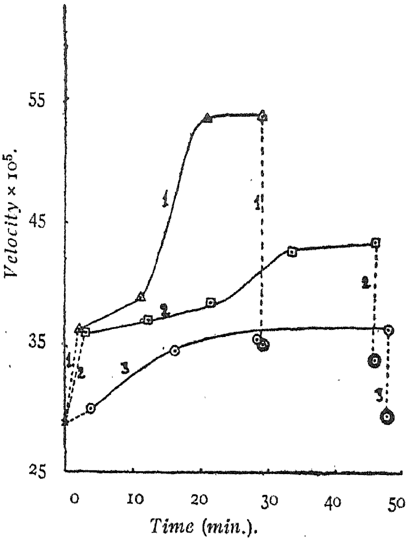
As_2S_3 *and palmitic acid sols.*



Curves 1 and 2 refer respectively to $As_2S_3 + N/7$-KCl and palmitic acid + $N/800$-$AlCl_3$.
O means C. V. after coagulation.

FIG. 4.

V_2O_5 *sol.*



Curves 1-3 refer respectively to $N/1500$-$BaCl_2$, $N/1000$-$AlCl_3$ and $N/15$-KCl.
O means C. V. after coagulation.

TABLE V.

Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
Water		7·643	10·63	8·38			
$N/2$-KCl	2-9 min.	15·03	24·31	17·32	16·03	24·3	18·7
	67-72	18·03	28·54	20·65			
	2-12	15·11	23·1	17·08			
	61-71	17·95	28·64	20·6			

Table V (contd.).

Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$	V.
$N/100$-$BaCl_2$	2-7	11·47	16·08	12·6			
	60-69	17·46	23·36	18·92	10·82	15·00	11·86
	126-128	16·92	23·69	18·61			
$N/800$-$AlCl_3$	2-7	16·03	27·68	18·94			
	17-21	21·04	31·39	23·63			
	24-26	22·22	31·9	24·63			
	36-39	25·36	35·32	27·85			
	56-59	26·02	34·04	28·02			
	3-8	16·32	27·35	19·07			
	18-24	21·26	24·73	22·12	19·1	21·3	19·6
	60-66	25·68	34·7	27·93			

Vanadium Pentoxide Sol.

Ammonium vanadate (5 g.) was triturated in a mortar with a few drops of hydrochloric acid. The red precipitate, thus obtained, was washed continuously on a Buchner filter until the filtrate assumed a red colour. The precipitate was washed further and the filtrate collected and transferred to a bottle and stirred with 200 c.c. of water. Within a few hours, a dark red colloidal solution was obtained which was fairly clear to transmitted light. Results are given in Table VI and illustrated in Fig. 4.

Table VI.

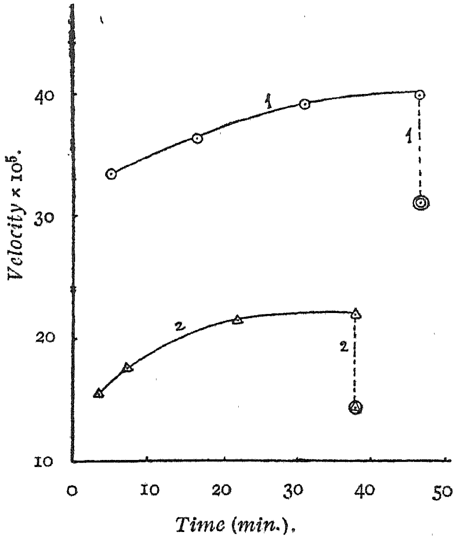
Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
Water		23·29	45·11	28·73			
$N/15$-KCl	2-6 min.	25·62	43·35	30·05			
	14-18	31·39	45·13	34·82	25·19	43·08	29·64
	27-30	32·39	45·8	35·68			
	47-49	33·34	46·7	36·68			
$N/1500$-$BaCl_2$	1-6	33·68	40·98	36·25			
	11-15	37·4	43·57	38·94	33·85	43·58	36·27
	20-25	51·45	62·85	52·3			
	1-3	34·4	42·48	36·42			
	9-13	37·33	43·98	38·98	33·36	42·22	35·57
	19-23	50·71	61·8	53·46			
	28-31	51·33	61·59	53·88			
$N/1000$-$AlCl_3$	1-5	34·24	42·86	36·39			
	9-16	34·9	44·5	37·26			
	20-23	36·34	45·64	38·66	30·48	45·27	34·17
	31-36	40·46	49·45	42·7			
	44-48	40·93	51·48	43·56			

Tungstic Acid Hydrosol.

From a solution of sodium tungstate, the oxide was precipitated by the action of hot concentrated HCl. The precipitate, so obtained, was filtered, washed with moderately dilute hydrochloric acid 3 or 4 times and once again with hot distilled water. With further washing the precipitate became peptised. The precipitate was then transferred to a bottle and suspended in water when it formed a sol. The peptised sol was dialysed in collodion sacs for a week with frequent changes of water and then electrodialysed for three days. Finally the sol was deposited by the current on the membrane and the supernatant water decanted off. The residue was now peptised with conductivity water and stocked in a bottle. The sol was coarsely dispersed and the larger particles settled down in a few days. Experiments were performed with portions of the sol pipetted out. The results are given in table VII and Fig. 5.

FIG. 5.

Tungstic acid sol.



Curves 1 and 2 refer respectively to $N/25$-KCl and $N/1000$-BaCl$_2$.
O means C. V. after coagulation.

TABLE VII.

Electrolyte.	Time after mixing.	Before coagulation.			After coagulation.		
		$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.	$V_{\frac{1}{6}}$.	$V_{\frac{1}{2}}$.	V.
Water		21·26	31·9	23·92			
$N/20$-KCl	2-7 min.	22·65	31·2	24·78			
	14-19	25·19	31·88	26·76	22·85	28·96	24·4
	25-33	26·53	32·51	28·02			
$N/25$-KCl	2-8	30·56	42·16	33·46	26·9	35·5	29·08
	14-19	34·31	42·18	36·28			
	27-35	36·09	48·39	39·15			
	44-49	37·11	48·35	39·92			
$N/1000$-$BaCl_2$	2-5	14·16	19·33	15·45			
	10-15	16·29	21·33	17·54	12·99	18·2	14·3
	20-24	20·62	24·07	21·46			
	32-46	21·18	24·26	21·93			

DISCUSSION.

The experimental results might be briefly summarised as follows :

(1) With arsenious sulphide hydrosol and potassium chloride, the c.v. increases with time to a value greater than the initial c.v. of the pure colloid. With barium chloride and aluminium chloride, though the c.v. is lower than that of the pure colloid, the c.v. here also increases with time in presence of a definite concentration of the electrolytes (*cf.* Fig. 2).

(2) With palmitic acid sol and the vanadium pentoxide hydrosol, the c.v. continually increases with time and is always higher than the initial c.v. of the pure colloid in presence of all the electrolytes. The initial c.v. of the palmitic acid sol is $8{\cdot}38 \times 10^{-5}$ cm./sec. per volt/cm., whereas that of the vanadium pentoxide hydrosol is $28{\cdot}7 \times 10^{-5}$ cm./sec. per volt/cm. (*cf.* Fig. 3 and 4).

(3) With tungstic acid sol also, the c.v. increases with time and is greater than that of the pure colloid with potassium chloride ; in presence of barium chloride, the c.v. is lower than the initial value but as aggregation proceeds, it increases with time (*cf.* Fig. 5).

(4) The c.v. of particles of a partially coagulated sol is lower than that of the sol before coagulation (*cf.* Fig. 2—5 and Tables III—VII).

(5) The c.v. of a colloid in presence of an electrolyte is smaller after the sol is centrifuged (*cf.* Table III ; *cf.* also Chaudhury, *J. Indian Chem. Soc.*, 1933, **10**, 431).

(6) If the c.v. of the large particles, which have settled during coagulation, be measured, being thoroughly shaken with the partially coagulated supernatant fluid, then it is found to be the same as that of the partially coagulated sol (*cf.* Table III). Results on points (4), (5) and (6) are tabulated below for the sake of clarity.

TABLE VIII.

		Cataphoretic velocity		
Sol.	Electrolyte.	Before coagulation.	After coagulation.	
Arsenious sulphide	*N*/6-KCl	43·75	35·2	
		45·78	33·54	
		44·39	34·96	
			36·2*	
	N/7-KCl	43·02	39·68	After centrifuging
		43·95	39·95	
		43·95	40·07	
		43·6	39·6	
	N/8-KCl	49·77	47·67	
	N/300-Ba Cl_2	21·06	17·54	
		21·98	17·67	
	N/350 ,,	21·01	18·53	
		22·02	18·6	
	N/400 ,,	20·03	17·23	
		20·85	17·27	
	N/1500-$AlCl_3$	23·09	13·46	
		23·73	13·27	
	N/3000 ,,	18·47	12·13	
Vanadium pentoxide	*N*/15-KCl	36·68	29·64	
	N/1500-$BaCl_2$	53·3	36.27	
		53·88	35·57	
	N/1000-$AlCl_3$	43·66	34·17	
Tungstic acid	*N*/20-KCl	28·02	24·4	
	N/25- ,,	39·92	29·08	
	N/1000-$BaCl_2$	21·93	14·3	
Palmitic acid	*N*/2-KCl	20·65	18·7	
	N/100-$BaCl_2$	18·61	11·86	
	N/800-$AlCl_3$	27·93	19·6	

* Supernatant coagulated sol thoroughly shaken with the original precipitate and c.v. measured.

These results are rather peculiar and they cannot be explained on the basis of any of the theories referred to. The outstanding facts that require to be explained, are :

(*i*) The increase of c.v. of a colloid with time in presence of an electrolyte at a concentration which produces an appreciable rate of coagulation.

(*ii*) That the increase in c.v. is due to the aggregation of the colloidal particles and not due to adsorption of ions of similar charge is evident from the fact that with salts having polyvalent cations of very low concentrations where the concentrations of anions are very small, the c.v. sometimes increases to a much greater extent than it does with uni-univalent salts.

Dependence of c.v. *on Size, Shape and Ionic Strength.*

According to the usual cataphoretic equation

$$V = \frac{\xi D X}{4\pi\eta} \qquad \ldots \quad (i)$$

where V is the cataphoretic velocity in cm. per volt/cm., ξ, the electrokinetic potential, D, the dielectric constant, X, the potential gradient in volts/cm., and η, the viscosity, the velocity should be independent of the size and shape of the particle and ξ, the electro-kinetic potential should determine the mobility. Debye and Hückel (*Physikal. Z.*, 1924, **25**, 49) on the other hand have deduced the relation

$$V = c.\frac{DX\xi}{\eta} \qquad \ldots \quad (ii)$$

where c, the constant, varies with the shape of the particle. In the case of a spherical particle, c is equal to $1/6\pi$, while for a cylinder it is $1/4\pi$. Henry (*Proc. Roy. Soc.*, 1931, **A**, **133**, 106) further points out that the value of the constant is $1/4\pi$, when the cylinder is placed axially to the applied field, but if it be placed broadside, c is $1/8\pi$. Moreover, the Debye equation is found by Henry to be true for spheres only when the electrical conductivity of the particle is identical with that of the medium. He also finds that in this case, the c. v. would depend on the shape of the particle. For an insulated particle, however, the Helmholtz-Smoluchowski equation is valid. Henry's actual equation is

$$u = \frac{3\mu}{2\mu + \mu'} \cdot \frac{DX\zeta}{6\pi\eta} \qquad \ldots \quad (iii)$$

He states "for an insulating sphere $\gamma' = o$ and $u = \frac{DX\xi}{4\pi\eta}$ in agreement with Smoluchowski's result, which is thus confirmed for a rigid spherical insulating particle subject to his four restrictions." μ and μ' are the specific conductances of the medium and the particle respectively and u, the mobility. In such a case, therefore, the cataphoretic velocity is independent of the shape and size of the particles. Henry (*loc. cit.*) further deduces the equation

$$V = \frac{X\sigma}{K} \cdot \frac{Ka}{1+Ka} \cdot (Ka) \qquad \ldots \quad (iv)$$

where V = mobility, σ = density of charge, a = radius of the colloidal particle, X = applied field and

$$K^2 = \frac{4\pi Ne^2}{1000DkT} \Sigma \gamma_i z_i^2$$

N is the Avogadro number, D, the dielectric constant, k the Boltzmann constant, T the absolute temperature, e, the charge of the electron in C. G. S. units and γ_i, the concentration per litre and z_i, the valency of the i th type.

To quote Henry again " we find that for values of Ka not less than 300, Smoluchowski's equation should hold to within 1%. For smaller values of Ka, if(Ka) diminishes towards the value $\frac{2}{3}$, until values of Ka about 0·5, Hückel's equation in turn becomes valid to within 1%. Provisionally, however, it may be inferred that particles in colloidal solutions will almost always lie in the region within which the cataphoretic velocity varies with the size but that droplets in emulsions and other suspended particles of microscopic size (as distinct from ultramicroscopic) should provide material for the experimental verification of Smoluchowski's equation." Henry (*loc. cit.*) gives the following table, showing the limits of diameter and of thickness of the ion atmosphere within which the Smoluchowski and Hückel equations are valid.

TABLE IX

(From Henry, *loc. cit.*)

Electrolyte.	Conc. (N).	K at 20° in cm^{-1}.	$1/K$ in μ.	Diameters.	
				S.	H.
Pure water		$1{\cdot}0 \times 10^{4}$	1·0	600	1·0
Uni-univalent	10^{-5}	$1{\cdot}0 \times 10^{5}$	0·1	60	0·1
	10^{-3}	$1{\cdot}0 \times 10^{6}$	0·01	6·0	0·01
	10^{-1}	$1{\cdot}0 \times 10^{7}$	0·0001	0·6	0·001
Uni-bivalent	10^{-5}	$1{\cdot}8 \times 10^{5}$	0·056	34	0·056
	10^{-1}	$1{\cdot}8 \times 10^{7}$	0·00056	0·34	0·00056
Bi-valent	10^{-5}	$2{\cdot}1 \times 10^{5}$	0·048	29	0·048
	10^{-1}	$2{\cdot}1 \times 10^{7}$	0·00048	0·29	0·00048

Muller (*J. Phys. Chem.*, 1931, **35**, 289) and Mooney (*ibid.*, 1931, **35**, 331) have attempted to explain the observations of Mooney (*loc. cit.*) as follows:

By applying the interionic attraction theory of Debye to colloidal particles Muller postulates that

$$\xi = \frac{4\pi\sigma}{D} \cdot \frac{1}{K} \cdot \frac{Ka}{1+Ka} \qquad \ldots \qquad (v)$$

and comparing it with the equation

$$\xi = \frac{4\pi\sigma}{D} \cdot d \qquad \ldots \qquad \ldots \qquad (vi)$$

where d is the thickness of the double layer and the other symbols have the same meaning as in equations (*ii*) and (*iv*), he gets the relation

$$d = \frac{1}{K} \cdot \frac{Ka}{1+Ka} \qquad (vii)$$

This formula shows that in general, the thickness of the double layer depends on the radius of the particle. This dependence of d on radius will manifest itself if Ka is small (*cf.* Henry, *loc. cit.*). Further when Ka is very large compared to unity, the cataphoretic velocity should become independent of the radius—conclusions which are similar to those drawn by Henry (*loc. cit.*). Mooney's experimental results are considered by Muller to agree with these conclusions, as large particles (where Ka is very large compared to unity) of nearly equal size having the most diverse shapes, move with a velocity in agreement with the theory of Smoluchowski, whenever the chemical constitution of the surface of the different particles is the same.

This theory is also considered to account for the observation of Mooney (*loc. cit.*) that with the addition of an electrolyte, the postulated increase in c. v. with increase in size, shifts to smaller radii and Abramsohn's observations that the c. v. of particles of microscopic size (1μ to 10μ approx.) are independent of the size for Ka now becomes sufficiently large. According to equation (*vi*) at a concentration of the electrolyte greater than 0·001 normal, particles of and above microscopic size (1μ to 10μ) should never show a variation of c. v. with size. Actually, however, we have found that such a variation occurs even for larger particles in solutions containing stronger electrolyte concentrations.

The limits of concentrations were from 0·001 N to 0·2 N. It follows from Table IX, given above that aggregates at such electrolyte concentrations should have a constant c. v. independent of size and shape and obey the Smoluchowski equation. Further, at such high ionic strengths, the c. v. should be small as the effective thickness of the ionic atmosphere must be small. Also, as the aggregation proceeds the shape should approximate a sphere assuming a chaotic arrangement of the primary particles and the c. v. should diminish. The observed increase in c. v. on aggregation contradicts all these deductions.

Considering the effect of an increase of the ionic strength it follows from the applications of the Debye-Hückel theory of strong electrolytes that the thickness of the double layer, or, of the ion atmosphere must diminish and the c. v. must decrease. But instead of a decrease, an increase has often been observed under such circumstances (Mukherjee, et al *loc. cit.*)

Another contradiction is afforded by the observation that the percentage increase in c. v. with time is greater in the case of the electrolytes having polyvalent precipitating ions which have a lower ionic strength. It follows from equations (*iv*) and (*v*) on the other hand, that the variation in c. v. with increase in the electrolyte concentration should diminish as the ionic strength diminishes, if the comparison is restricted to the aggregation of the same set of particles (Mukherjee, Chaudhury and Ghosh, *loc. cit.*). It is obvious that all these theories ignore the part played by the specific character of the surface and the adsorption of ions.

The general picture of the changes brought about by the addition of an electrolyte and the consequent aggregation of the particles in the equilibrium distribution of ions in the double layer surrounding the primary particles have been visualised before (Mukherjee, Chaudhury and Ghosh, *loc. cit.*). These changes can be stated as follows in detail:

(*a*) Changes in the distribution of the ions in the double layer surrounding the primary particles which may affect the primarily adsorbed, the electrically adsorbed ions, and those in the mobile layer.

(*b*) Rearrangement of the above distribution resulting from the aggregation of the colloidal particles (assuming no change in the surface of the primary particles forming the aggregate) which involves a diminution in the capacity. The aggregation may also involve an increase in the surface density of the charge in the neighbourhood of the surface of aggregation.

(*c*) A net diminution in the interface may result from the coalescence at the particular spots of the aggregating particles. This would increase the surface density of the charge and the potential if the fixed layer of adsorbed ions is not affected by coalescence. On the other hand the fixed adsorbed ions at such places with their mobile particles may be set free as a result of the coalescence. Perhaps, this happens when precipitation takes place and with which is associated the sudden drop in the potential.

(*d*) An entrainment of ions serving as links between the primary particles, which unite them into the aggregate, may also happen.

The considerations advanced above have an important bearing on problems in several branches of science, *e.g.*, the formation of soil aggregates. It has been observed that the effect of (*a*) is often to increase the c. v. if the initial density of the charge of the colloid is low, specially with univalent coagulating ions (*cf.* Figs. 2, 4, 5 and Table V) and sometimes even with divalent or trivalent coagulating ions (*cf.* Fig. 4 and Table V). With divalent or trivalent precipitating cations, the electrical adsorption should predominate. The c. v. would diminish on the addition of the electrolyte but it has been observed (*vide* Figs. 2, 3, 4, 5) that the c. v. increases with aggregation in this case also. Moreover, the c. v. on the addition of electrolytes with divalent and trivalent cations is in several instances (*vide* Tables III to VIII) greater than that of the pure colloid. These observations dispose of the arguments often advanced (Kruyt and Willizen, *Kolloid Z.*, 1928, **44**, 22) to explain away the high coagulating potentials observed with univalent coagulating ions. It is maintained that there is a critical coagulating potential in the case of electrolytes which coagulate at low concentrations and that the higher potential observed with univalent coagulating ions is an exception arising out of the adsorption of ions of same sign or out of the decrease of the dielectric constant at such high concentrations. This argument also overlooks the higher potential itself, as the stability is assumed to be directly determined by the potential, no matter what the causal factors are. In several instances, the percentage increase in c. v. is greater for the bi- or trivalent than with the univalent precipitating ions. The magnitude of the change in c. v. appears to depend on the cation and on the sol. It is possible that the polyvalent cations, which are known to produce coagula in which the primary particles are more firmly bound, bring the surfaces of the primary particles in closer contact and hence enhance the potential.

Apart from these considerations, there might be an increase in the c. v. due to endosmosis set up in the cell as a result of the net work structure of the coagula in the cell. But these and other considerations await further experimental results before any definite conclusion as to the effect it produces can be arrived at.

SUMMARY.

1. It has been shown that the c. v. of a colloid increases with time, *i.e.*, with the process of aggregation of the colloidal particles in presence of an electrolyte.

2. This effect, *i.e.*, the increase in c. v. with time, is more marked, the higher the valency of the precipitating ions. Sometimes the c. v. rises to a much higher value than that of the colloid itself with di- or trivalent precipitating ions.

3. The c. v. of the supernatant suspension of a colloid after partial coagulation is less than that of the colloid before coagulation.

4. The c. v. of the coagula (in the case of As_2S_3 sol) is the same as that of the supernatant suspension of the colloid after coagulation.

5. These results are not in accord with the theories of cataphoresis as developed by Helmholtz, Smoluchowski, Debye and Hückel and Henry and Mooney. A tentative suggestion based on the considerations of Mukherjee's theory of ion adsorption and of the aggregation of the colloidal particles has been advanced.

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Peroxidases. Part III. A Potentiometric Method of Estimating their Activity.

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The observation was made sometime ago (Dey and Sitharaman, *J. Indian Chem. Soc.*, 1931, **9**, 479) that hydroquinone was oxidised to quinhydrone by peroxidase in presence of hydrogen peroxide, and on the basis of this observation a method for estimating the peroxidase activities of plant saps was elaborated (*loc. cit.*). In that method a known weight of hydroquinone and a known amount of hydrogen peroxide were taken along with the necessary buffer, a fixed volume of peroxidase solution or sap added and the mixture stirred for a definite period, the reaction vessel being kept at 10-13° throughout the experiment. After the reaction was inhibited by the addition of hydrochloric acid, the liquid was quickly filtered through an Allihn tube, the precipitate of quinhydrone dissolved in a mixture of alcohol and hydrochloric acid (1:1), a solution of potassium iodide added and the liberated iodine titrated against standard thiosulphate using starch as an indicator. A correction for the quinhydrone lost had to be made by carrying out a blank with a known amount of quinhydrone and without the hydrogen peroxide under identical conditions. The correction applied was, therefore, empirical. No knowledge as to whether the hydrogen peroxide had reacted completely, or not was obtainable, nor was it possible to say if the amount of hydrogen peroxide that had disappeared corresponded with the amount of oxidation of the substrate.

The present investigation has been undertaken with the object of supplying this deficiency by applying potentiometric methods for the determination of (*a*) the substrate, (*b*) the hydrogen peroxide left over and (*c*) the quinhydrone formed. Thus the loss of quinhydrone during the operations of filtration and washing involved in the previous processes might be avoided.

The use of ceric sulphate in the determination separately of hydrogen peroxide and hydroquinone by Furman and Wallace (*J. Amer. Chem. Soc.*, 1929, **51**, 1449; 1930, **52**, 1443) had encouraged the hope at the beginning that the same reagent could be employed for estimating the two substances in the peroxidase reaction mixture. The problem did not appear, however, to be very simple, the chief difficulty encountered being that of determining the end-point accurately. In fact no sharp end-point could be recognised on titrating mixtures of known amounts of hydrogen peroxide and hydroquinone against ceric sulphate, the potential changing continuously without showing any break even at the point corresponding to the stage of oxidation of both hydrogen peroxide and hydroquinone. Attempts made by using different electrode systems, to counteract the influence of polarisation caused chiefly by the quinone formed as a result of the oxidation of hydroquinone, did not lead to any improvement. It was found in the course of these experiments that the reaction between ceric sulphate and hydrogen peroxide was dependent on the hydrogen-ion concentration and in solutions, where the latter was reduced by sodium acetate, the reaction became practically nil, although under the same conditions, the hydroquinone was quantitatively oxidised (*vide* Table I). When these estimations were carried out with mixtures, however, no end-point was discernible either at the stage corresponding to the individual oxidation of hydroquinone or of the complete reaction of both.

Attention was next directed to the possibility of determining the hydroquinone alone in the reaction mixture after destruction of the hydrogen peroxide left over by means of catalase extracts. The latter were prepared from ox-kidney according to the method described by Morgulis and co-workers (*J. Biol. Chem.*, 1926, **58**, 521). Here, too, no satisfactory end-point could be reached and it was noticed in a blank experiment carried out with the sap alone that the plant sap itself consumed considerable quantities of the ceric sulphate, which was a powerful oxidising agent. No definite end-point could be obtained, however, even for the titration of the blank. The use of ceric sulphate as an oxidant had, therefore, to be ultimately abandoned on account of these difficulties. The failure is very probably caused by the fact that the oxidation potential of hydrogen peroxide is an uncertain factor, and in a mixture of hydrogen peroxide and hydroquinone the difference in oxidation potentials of the two substances might be so small that no selective oxidation was possible with the consequence that both were simultaneously oxidised.

Attempts were next made to destroy the excess of hydrogen peroxide by adding catalase and then estimating (*i*) the quinhydrone formed by thiosulphate in acetic acid medium (Rzymkowski, *Z. Elektrochem.*, 1925, **31**, 371) and (*ii*) the excess of hydroquinone left over by potassium dichromate in dilute sulphuric acid medium in another aliquot part (Kolthoff, *Rec. trav. chim.*, 1926, **45**, 745). These experiments have been entirely successful and have led to the development of a reliable potentiometric method for estimating the peroxidase activities of plant saps.

EXPERIMENTAL.

About 0·3 g. of pure hydroquinone (Kahlbaum) was weighed accurately into a dry, clean boiling tube and the test tube placed in powdered ice in a Dewar flask. 5 C.c. of buffer consisting of sodium acetate and hydrochloric acid of p_H 4·58, which is in the optimal p_H region for the reaction (*cf.* Dey and Sitharaman, *J. Indian Chem. Soc.*, 1932, **8**, 499) and 2 c.c. of 1% hydrogen peroxide were added and the liquid stirred vigorously with a mechanical stirrer while 5 c.c. of the sap were added. The time is noted when the addition is over, and precisely at the end of 15 minutes, 5 c.c. of 1·0*N* hydrochloric acid was added to inhibit the reaction. A minute later 5 c.c. of 1·0*N* sodium acetate solution were added to neutralise the hydrochloric acid and yet another minute later 1 c.c. of catalase extract. The reaction was allowed to proceed for 15 minutes at the end of which the liquid was made up to 100 c.c. with freshly boiled distilled water at the laboratory temperature.

A blank exactly as above but without the hydroquinone was carried out and the liquid made up to 100 c.c. in the same way.

20 C.c. of each were titrated against standard potassium dichromate using normal calomel electrode and a platinum electrode in a solution of about 1·5*N* sulphuric acid. The platinum electrode was ignited after every titration in a spirit lamp flame.

The enzyme-reacted solution (40 c.c. or 60 c.c. as the case may be) was titrated against standard sodium thiosulphate. The electrode system employed at first was gold and platinum (*cf.* experiments with horse radish sap), but was later changed with advantage to a system of gold and Veibel's quinhydrone electrode (*J. Chem. Soc.*, 1923, **123**, 1103). The liquid was about 2*N* with respect to acetic acid and the titrant in this case was added drop by drop. The equilibrium potential was attained pretty quickly in the early stages of the titration but near the equivalence point it was found to take longer time to attain equilibrium.

The results of the experiments are given in Tables II, III and IV. Titrations with thiosulphate give the quinhydrone (quino part alone) calculated as hydroquinone oxidised (1 mol. of quinone = 1 mol. of hydroquinone). Titrations with dichromate after correction for blank give the hydroquinone left over unoxidised. (In this is included the hydroquinone part of quinohydrone). The sum of these two quantities must be equal to the hydroquinone taken. As may be seen from the tables, the values obtained for the total hydroquinone from the titrations agree well with the weight actually taken for the experiments, the experimental error being less than 1 %.

TABLE I (*a*).

15 C.c. of hydroquinone soln., 25 c.c. of 4*N*-HCl and 60 c.c. of water titrated against ceric sulphate using platinum and normal calomel electrodes. Vol. at the equiv. point = 12·05 c.c.

Voltage ...	0·2520	0·4545	0·4699	0·7455	0·7717
Burette reading ...	17·17	29·20	29·25	29·30	29·35

TABLE I (*b*).

15 C.c. of hydroquinone solution, 25 c.c. of 1·0*N*-sodium acetate solution and 60 c.c. of water titrated against ceric sulphate using platinum and normal calomel electrodes. Vol. at equiv. point = 12·15 c.c.

Voltage ...	0·0260	0·1175	0·1335	0·1575	0·1850	0·2315	0·2410	0·2575	0·3155	0·3520	0·3705
Burette reading ...	29·35	34·35	36·35	38·35	40·35	41·35	41·40	41·45	41·50	41·55	41·60

These results show that the potentiometric determination of hydroquinone using ceric sulphate as the oxidant proceeds equally well in hydrochloric and in acetic acid medium. In the case of hydrogen peroxide, the estimations could be carried out satisfactorily in hydrochloric acid medium, the potentials being found to conform to the observations of Furman and Wallace (*loc. cit.*). When, however, the titrations were done in sodium acetate medium, it became clear that the reaction was not proceeding at all since there was no decolourisation, and after some time the ceric sulphate was hydrolysed.

A series of blanks carried out without hydrogen peroxide with the three saps, conditions being the same, both at 0° and at 13° shows that the influence of dehydrogenases, even if present, is practically nil, but the lower temperature was chosen chiefly on account of convenience. The following are the results obtained.

TABLE II.

	Results at 0°		Results at 13°	
Sap.	H.Q. taken.	H.Q. found.	H.Q. taken.	H.Q. found.
Horse radish	0·2976	0·2974	0·3030	0·3024
Chow-chow	0·2992	0·2986	0·2984	0·2978
Red radish	0·2982	0·2978	0·2976	0·2978

TABLE III(*a*).

Experiments with horse-radish (Raphanus sativus) (sap not dialysed).

EXPERIMENT I.

Wt. of hydroquinone taken = 0·3015 g. 40 C.c. of the enzyme-reacted solution against 0·04806*N*-$Na_2S_2O_3$. Au-Pt electrode system.

Voltage	...	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·0068	0·0070
Burette reading	...	15·55	16·55	17·55	18·55	19·05	20·05	20·55	20·65	20·70	20·75

(The voltage indicated was zero until very near the end-point, when there was a sudden and sharp rise in potential which hardly changed at all on further addition of the reagent. The approach near the end-point was easy to recognise from the tendency shown by the galvanometer to indicate a rise in voltage.)

TABLE III (*b*).

20 C.c. of the enzyme-reacted solution against 0·1039*N*-$K_2Cr_2O_7$. Pt—*N*-calomel electrodes.

Voltage.	Burette reading.		$\Delta E/\Delta C$ (m.volt/c.c.).
0·4363	27·05		164
0·4445	27·10		310
0·4600	27·15		640
0·4920	27·20	... 8·40 c.c.	
0·5215	27·25		590
0·5495	27·30		560
0·5730	27·35		470

TABLE III(*c*).

20 C. c. of blank solution under the same conditions of acidity as above, *viz.*, 2N with respect to H_2SO_4 against 0·1039N-$K_2Cr_2O_7$. Pt—N- calomel electrodes.

H. Q. taken = 0·3015 g.

H. Q. corresp. to $K_2Cr_2O_7$ titration = 0·2358 g.

H. Q. corresp. to $Na_2S_2O_3$ titration = 0·0682 g.

Calc. value for total H. Q. = 0·3040 g.

Voltage.	Burette reading.	$\Delta E/\Delta C$ (m.volt/c.c.)
0·3810	27·40	230
0·3925	27·45	300
0·4075	27·50	360
0·4255	27·55 ... 0·15 c.c.	
0·4390	27·60	270
0·4465	27·65	150
0·4530	27·70	130

TABLE IV.

Experiments with horse-radish (R. sativus) (sap not dialysed).

	Expt. II.	Expt. III.
Hydroquinone taken ...	0·2976 g.	0·2988 g.
H. Q. unreacted (from $K_2Cr_2O_7$ titration) ...	0·2325	0·2501
H. Q. reacted (from thiosulphate titration) ...	0·0635	0·0415
Total H. Q. (found from expt.) ...	0·2950	0·2986
Electrode system used ...	Au/Pt Pt—N- cal.	Au/Pt Pt—N- cal.
Limit of accuracy ...	—0·87 %	—0·067 %

TABLE V(*a*).

Experiments with chow-chow (Sechium edule) (sap dialysed).

Wt. of H. Q. taken = 0·2950 g. 40 C. c. enzyme-reacted soln. against 0·04806 N-$Na_2S_2O_3$. Au-Veibel's quinhydrone electrodes.

Voltage.	Burette reading.	$\Delta E/\Delta C$ (m.volt/c. c.).
0·0679	36·00	
0·0729	36·05	
0·0805	36·10	210
0·910	36.15	308
0·1064	36·20 ... 4·60 c. c.	
0·1185	36·25	242
0·1265	36·30	160

TABLE V(*b*).

20 C. c. enzyme-reacted solution against 0·1039 N-$K_2Cr_2O_7$. Pt-N-calomel electrodes.

Voltage.	Burette reading.			$\Delta E/\Delta C$ (m.volt/c.c.).
0·3585	28·50			
—	—			
0·4759	36·65			328
0·4923	36·60			974
0·5410	36·65	...	8·15 c.c.	
0·5538	36·70			256

TABLE V(*c*).

20 C. c. blank solution against 0·1039 N-$K_2Cr_2O_7$. Pt—N-calomel electrodes.

H. Q. taken =0·2950 g.

H. Q. corresp. to $K_2Cr_2O_7$ titration =0·2315 g.

H. Q. corresp. to $Na_2S_2O_3$ titration =0·0608 g.

Calc. value for total H. Q. =0·2923 g.

Voltage.	Burette reading.			$\Delta E/\Delta C$ (m.volt/c.c.
0·4865	28·30			110
0·4920	28·35	...	0·05 c.c.	
0·4958	28·40			76
0·4976	28·54			36

TABLE (V*d*).

Experiments with chow-chow, (Sechium edule) (sap dialysed).

In this series of experiments, combination of Veibel's quinhydrone and gold electrode gave better results in the estimation of quinhydrone by thiosulphate, the end-point being sharper. The hydroquinone was estimated using Pt/N-cal. combination.

	Expt. II.	Expt. III.
H. Q. taken	0·2959	0·2914
H. Q. (unreacted)	0·2386	0·2372
H. Q. reacted	0·0555	0·0536
Total H. Q. (found)	0·2941	0·2908
Electrode system	Au/Veibel Pt/N- cal.	Au/Veibel Pt/N- cal.
Limits of accuracy	−0·6%	−0·2%

TABLE VI (*a*).

Experiments with red radish (Raphanus sativus) red variety.

In expt. I the undialysed sap was used; in expt. II and III the dialysed sap was used.

EXPERIMENT I.

Wt. of H. Q. taken = 0·2984 g. 40 C.c. of enzyme-reacted soln. against 0·04806N-$Na_2S_2O_3$. Au/Veibel's quinhydrone electrodes.

Voltage.	Burette reading.		$\Delta E/\Delta C$ (m.volt/c.c.).
0·0245	29·90		
—	—		
0·0965	34·70		
			220
0.1075	34·75		
			330
0·1240	34·80	...4·90 c.c.	
			230
0·1355	34·85		

TABLE VI (*b*).

20 C.c. enzyme-reacted soln. against 0·1039 N-$K_2Cr_2O_7$. Pt/N-cal. electrodes.

Voltage.	Burette reading.		$\Delta E/\Delta C$ (m.volts/c.c.).
0·3567	31·50		
...	...		
0·4490	39·45		
			386
0·4683	39·50		
			724
0·5045	39·55	...8·05 c.c.	
			340
0·5215	39·60		

TABLE VI (*c*).

20 C.c. blank solution against 0·1039 N-$K_2Cr_2O_7$. Pt/N-cal. electrodes.

Voltage.	Burette reading.		$\Delta E/\Delta C$ (m.volt/c.c.).
0·2550	31·30		
			510
0·2805	31·35		
			600
0·3105	31·40	...0·10 c.c.	
			490
0·3350	31·45		
			250
0·3475	31·50		

H. Q. taken ...	0·2984 g.
H. Q. corresp. to $K_2Cr_2O_7$ titration ...	0·2272 g.
H. Q. corresp. to $Na_2S_2O_3$ titration ...	0·0646 g.
Calc. value for total H. Q. ...	0·2918 g.

(This is the only case where the error exceeds 1%, possibly because the sap was not dialysed. In experiments II and III where the sap had been dialysed before use, the error does not exceed 1%).

TABLE VI (*d*).

Experiments with red radish (Raphanus sativus).

In experiment I, the undialysed sap was used and in experiments II and III, the dialysed sap was used.

	Expt. II.	Expt. III.
H. Q. taken	0·2968	0·3006
H. Q. unreacted	0·2272	0·2344
,, ,, reacted	0·0666	0·0633
Total H. Q. (found)	0·2938	0·2977
Electrode system	Au/Veibel Pt/*N*-cal.	Au/Veibel Pt/*N*- cal.
Limit of accuracy	−1%	−0·98%

The high error may be due to undialysed sap.

In the titration, where the quinhydrone was titrated against $Na_2S_2O_3$ using Veibel's quinhydrone electrode, a salt bridge was used for the electrode.

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New Compounds of Gallium. Part I.

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Existing literature shows that only a few compounds of gallium are actually known. We have been fortunate in securing a tolerably large quantity of this rare metal and thus have been enabled to prepare many of its commoner inorganic and organic salts, which have hitherto been unknown.

A hydrate of the formula Ga_2O_3, $3H_2O$ is known but we have been able to prepare another hydrate having the formula Ga_2O_3, $2H_2O$. The former is obtained when the hydroxide is freshly precipitated from the nitrate by the action of sodium bicarbonate and is readily soluble in organic and inorganic acids. This compound, however, loses the property of dissolving in organic acids when it is kept overnight, and on drying in a vacuum desiccator has the composition Ga_2O_3, $2H_2O$ corresponding to Al_2O_3, $2H_2O$. This property is shared by aluminium hydroxide also, which, when freshly prepared, dissolves easily in acids and in alkaline hydroxides, whilst Al_2O_3, $2H_2O$ is almost insoluble in dilute acids and alkalis.

Basic gallium acetate having the formula $5Ga(CH_3CO_2)_3$, $2\,Ga_2O_3$, $5H_2O$ was prepared by Tchakirian (*Compt. rend*, 1929, **189**, 251) by adding 30% excess of acetic acid to a solution of a gallium salt neutralised with ammonium carbonate. Two basic acetates have been prepared, one having the same formula as the above compound but prepared by dissolving the freshly prepared hydroxide in acetic acid. The other compound was prepared by adding sodium acetate to a solution of gallium nitrate and possessed the formula,

$$Ga(CH_3COO)_3,\ 3Ga_2O_3,\ 6H_2O.$$

A gallium tartrate is mentioned in a pharmaceutical paper (*Compt. rend*, 1931, **192**, 1142) but no mention has been made either of the composition or its method of preparation. We have prepared all the four tartrates of gallium, *d*, *l*, and *racemic* as well as the *meso* compound and have also determined the specific rotations of the *dextro* and the *laevo* componnds.

A normal oxalate of gallium of the formula $Ga_2(C_2O_4)_3, 4H_2O$ was prepared by Tchakirian (*loc. cit.*) by boiling a solution of gallium nitrate and oxalic acid in presence of sufficiently concentrated nitric acid to destroy the excess of oxalic acid, which otherwise dissolves the oxalate. We have prepared the same compound by dissolving freshly prepared gallium hydroxide in solution of oxalic acid. A basic oxalate of the formula $Ga_2(C_2O_4)_3, 3Ga_2O_3, 7H_2O$ has been obtained by adding sodium oxalate to a solution of gallium nitrate. The other compounds mentioned in this paper are new ones.

As regards analysis of the salts, organic salts were analysed by igniting them to the oxide and then weighing it. The initial heating was done very carefully in order to avoid charring as much as possible. In the case of inorganic salts, the hydroxide was first precipitated which was subsequently ignited to the oxide. In the case of soluble salts like the acid hypophosphite of gallium, it was dissolved in water and the solution boiled with solid hydrated sodium sulphite to precipitate the hydroxide (Dennis and Bridgeman, *J. Amer. Chem. Soc.*, 1918, **40**, 1544). In the case of insoluble salts such as acid gallium phosphite, gallium phosphite and gallium hypophosphite, these were dissolved in hydrochloric acid and to the chloride solutions were added solid ammonium chloride and ammonia in excess. The solution was boiled till the excess of ammonia was removed when the precipitation of the hydroxide was completed as shown by Dennis and Bridgeman (*loc. cit.*). The filtrates did not contain any gallium and the precipitate no phosphorus compound.

The water was estimated by keeping a weighed quantity in an air oven heated to 100°-110°.

EXPERIMENTAL.

Gallium Hydroxides ($Ga_2O_3, 3H_2O$ and $Ga_2O_3, 2H_2O$).

Pure metallic Ga was dissolved in concentrated nitric acid by slow heat. The excess of nitric acid was evaporated to dryness. The nitrate was dissolved in water and the solution heated to boiling and to the hot solution, hot dilute solution of sodium bicarbonate was added drop by drop with constant stirring till the precipitation was complete. The white gelatinous precipitate was washed several times with hot water and then thoroughly dried in air between filter papers. (Found : Ga, 58·15 ; H_2O, 21·84. $Ga_2O_3, 3H_2O$ requires Ga, 57·85; H_2O, 22·31 per cent).

The precipitated and washed hydroxide was kept in a vacuum desiccator until thoroughly dried when the hydrate with two molecules of water was obtained (Found: Ga, 62·76; H_2O, 15·63. $Ga_2O_3, 2H_2O$ requires Ga, 62·50; H_2O, 16·07 per cent).

Gallium d, l, r, *and* meso-*Tartrates.*

Freshly prepared gallium hydroxide was just dissolved in aqueous solutions of the respective tartaric acids and solutions of the tartrates thus obtained were left in a vacuum desiccator for crystallisation. The salts were washed several times with alcohol in order to remove the free tartaric acids. All the tartrates were found to have the composition, $Ga_2(C_4H_4O_6)_3, 4H_2O$ and were white crystalline substances, soluble in water but insoluble in alcohol and ether.

Gallium d-*Tartrate*. [Found: Ga, 21·30; H_2O, 10·79. $Ga_2(C_4H_4O_6)_3, 4H_2O$ requires Ga, 21·34; H_2O, 10·97 per cent]. Sp. rotation in 1 dcm. tube = +20·3° and $[M] = +133{\cdot}1$.

Gallium l-*Tartrate*. [Found : Ga, 21·03 ; H_2O, 11·05. $Ga_2(C_4H_4O_6)_3, 4H_2O$ requires Ga, 21·34; H_2O, 10·97 per cent]. Sp. rotation in 1 dcm. tube = −20·0° and $[M] = -131{\cdot}2^\circ$.

Gallium Racemate. [Found: Ga, 21·07 ; H_2O, 11·17. $Ga_2(C_4H_4O_6)_3, 4H_2O$ requires Ga, 21·34; H_2O, 10·97 per cent]. The salt was found to be optically inactive.

Gallium meso-*Tartrate*. [Found : Ga, 21·04; H_2O, 10·85. $Ga_2(C_4H_4O_6)_3, 4H_2O$ requires Ga, 21·34; H_2O, 10·97 per cent]. The salt was found to be optically inactive.

Basic Gallium Acetate was deposited slowly as white hygroscopic micro-crystals from a solution of freshly prepared gallium hydroxide in dilute acetic acid, avoiding excess of the acid. The substance was repeatedly washed with alcohol in order to free it from the acid and then analysed by ignition to the oxide. The salt was found to be insoluble in water, alcohol and ether but soluble in dilute hydrochloric acid. [Found : Ga, 38·30; H_2O, 6·45. $4Ga(CH_3CO_2)_3, 2Ga_2O_3, 5H_2O$ requires Ga, 38·51; H_2O, 6·18 per cent].

Basic Gallium Formate was obtained as a white crystalline substance by just dissolving the freshly prepared hydrate in dilute solution of formic acid and keeping it in a vacuum desiccator overnight. The salt was purified by washing with alcohol. The salt is insoluble in water, alcohol and ether but soluble in dilute hydrochloric acid.

[Found : Ga, 42·96; H_2O, 17·96. $Ga(HCO_2)_3$, Ga_2O_3, $5H_2O$ requires Ga, 43·47; H_2O, 18·63 per cent]. The same salt was obtained by adding a solution of sodium formate to gallium nitrate solution, when a white precipitate was obtained. It was washed several times with hot water, dried and on analysis gave the identical composition. [Found : Ga, 43·94; H_2O, 19·15. $Ga(HCO_2)_3$, Ga_2O_3, $5H_2O$ requires Ga, 43·47; H_2O, 18·63 per cent].

Normal Gallium Oxalate was prepared by just dissolving the freshly precipitated gallium hydroxide in a solution of oxalic acid. The solution on keeping in a vacuum desiccator yielded a white micro crystalline substance which was purified by repeated washing with a mixture of alcohol and ether. The salt is a hygroscopic, microcrystalline powder, readily soluble in water and moderately so in alcohol but insoluble in ether. [Found : Ga, 29·36; H_2O, 14·77. $Ga_2(C_2O_4)_3$, $4H_2O$ requires Ga, 29·41; H_2O, 15·12 per cent].

Gallium Citrate was prepared by dissolving the freshly precipitated hydroxide in dilute solution of citric acid, crystallised in a vacuum desiccator and purified by washing with alcohol. It is a white crystalline powder soluble in water but insoluble in alcohol and ether. [Found : Ga, 21·81; H_2O, 16·41; $Ga(C_6H_5O_7)$, $3H_2O$ requires Ga, 22·36; H_2O, 17·25 per cent].

Gallium Lactate was obtained in the same way by dissolving gallium hydroxide in dilute solution of lactic acid, crystallised and purified by washing with ether. Gallium lactate is a white microcrystalline powder soluble in water, moderately so in alcohol but insoluble in ether. [Found : Ga 18·65; H_2O, 10·31. $Ga(C_3H_5O_3)_3$, $2H_2O$ requires Ga, 18·76; H_2O, 9·65 per cent].

Gallium Malate was prepared by dissolving freshly precipitated gallium hydroxide in malic acid solution, crystallising in a vacuum desiccator and washing with alcohol. Gallium malate is a white crystalline substance soluble in water but insoluble in alcohol and ether. [Found : Ga, 23·67; H_2O, 9·75. $Ga_2(C_4H_4O_5)_3$, $3H_2O$ requires Ga, 23·72 ; H_2O, 9·15 per cent].

Acid Phosphite of Gallium was obtained by dissolving the freshly precipitated gallium hydroxide in dilute solution of phosphorous acid, evaporating to dryness in a vacuum desiccator and purified by washing with alcohol. The acid phosphite of gallium is a white crystalline powder, insoluble in water, alcohol and ether, but soluble in dilute hydrochloric acid. [Found : Ga, 28·60; H_2O, 8·06. $GaH_3(PO_3)_2, H_2O$ requires Ga, 28·11; H_2O, 7·22 per cent].

Normal Phosphite of Gallium.—When a solution of sodium phosphite was added to gallium nitrate solution, the white precipitate of the normal phosphite was obtained which was purified by washing with hot water and dried. The salt is insoluble in water, alcohol and ether, but soluble in dilute hydrochloric acid. (Found : Ga, 41·55; H_2O, 11·62. $GaPO_3, H_2O$ requires Ga, 41·91; H_2O, 10·78 per cent).

Acid Hypophosphite of Gallium was prepared exactly as the acid phosphite by dissolving the freshly precipitated gallium hydroxide in hypophosphorous acid. The substance was dried and washed with alcohol. The salt is a white powder, soluble in warm water, but insoluble in alcohol and ether. [Found : Ga, 34·34. $GaH_3(PO_2)_2$ requires Ga, 36·17 per cent].

Normal Hypophosphite of Gallium was obtained as a white precipitate by adding sodium hypophosphite to the solution of gallium nitrate. The precipitate was washed with hot water and dried. The salt is insoluble in water, alcohol and ether but soluble in dilute hydrochloric acid. (Found : Ga, 45·49; H_2O, 11·18. $GaPO_2, H_2O$ requires Ga, 46·35; H_2O, 11·92 per cent).

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Oxidation of Acetyltetrahydroquinoline Sulphonic Acids.

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While studying the derivatives of cresol sulphonic acids and sulphohydroxybenzoic acids, attempts were previously made in this laboratory to synthesise 6-sulphosalicylic acid without success.

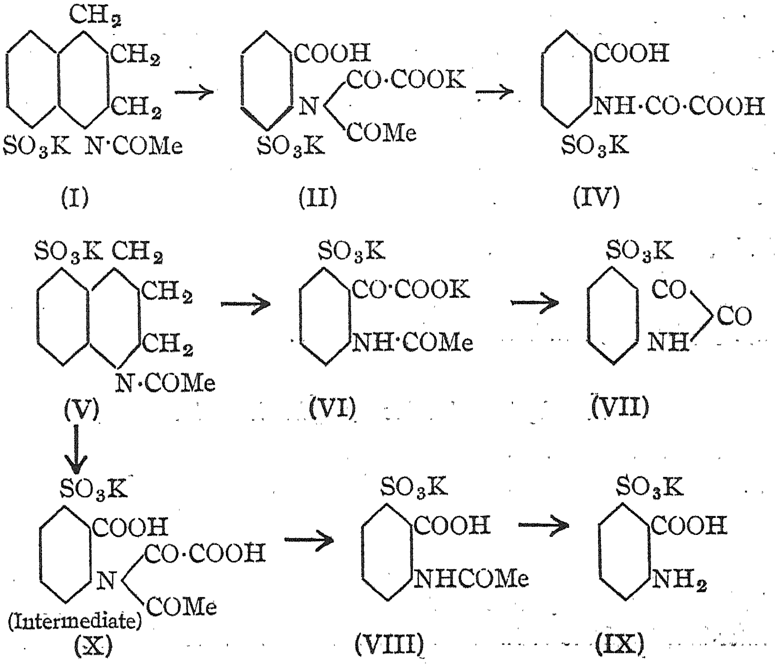
A new line of attack was suggested by the work of Zürcher (*Ber.*, 1888, **21**, 180) who recognised the formation of 2-amino-3-sulphobenzoic acid (very small yield). In the oxidation products of quinoline-8-sulphonic acid (Fischer and Renouf, *Ber.*, 1884, **17**, 755) Zürcher's acid was converted into the corresponding sulphosalicylic acid by Sucharda (*Chem. Zentr.*, 1927, **1**, 3005). An attempt was, therefore, made to see whether the isomeric quinoline-5-sulphonic acid could be oxidised to yield the corresponding 2-amino-6-sulphobenzoic acid (or its derivative), which may ultimately be converted into the required sulpho-salicylic acid. The attempt was, however, unsuccessful; only the formation of quinolinic acid, obtained by Fischer (*loc. cit.*), could be recognised.

It was, however, thought possible to get the derivatives of the amino-sulpho acids as main products of oxidation, if the quinoline sulphonic acids were first reduced, acetylated and then oxidised. The reduction was carried out with tin and hydrochloric acid, and the potassium salts of the tetrahydroquinoline sulphonic acids, thus obtained, could be easily acetylated by heating with acetic anhydride.

The oxidation of potassium acetyltetrahydroquinoline-8-sulphonate (I) with aqueous potassium permanganate at the ordinary temperature, gives a 60% yield of the acid dipotassium salt of 2-oxalyl-acetylamino-3-sulphobenzoic acid (II), and also a small quantity of the corresponding acid monopotassium salt (III). The compound (II) on heating for sometime with HCl solution (1:2), yields the acid monopotassium salt of 2-oxalylamino-3-sulphobenzoic acid (IV); but this, as well as the compound (II), gets decomposed by heating with concentrated hydrochloric acid. Potassium tetraoxalate was, however, recovered and identified and the dark bluish-red solution, on dilution with water, gives the characteristic blue flurorescence of the free amino-sulpho-acid which could not be recovered.

Oxidation of potassium acetyltetrahydroquinoline-5-sulphonate (V) under the same conditions (a very slow reaction) is found to proceed in two different directions. The major product is the dipotassium salt of 2-acetylamino-6-sulphobenzoylformic acid (VI), which when warmed with concentrated hydrochloric acid gives the potassium salt of the hitherto unknown isatin-4-sulphonic acid (VII). The preparation of free isatin sulphonic acid will be described in a separate communication.

The other substances obtained in small quantities are acid potassium salt of 2-acetylamino-6-sulphobenzoic acid (VIII) and probably the acid potassium salt of 2-amino-6-sulphobenzoic acid (IX) (*vide* experimental). The quantity of the last substance was very small and hence could not be thoroughly investigated. Potassium tetraoxalate was, however, recovered and identified showing that the oxidation in the direction of the intermediate formation of a compound (X) must have taken place, giving finally by further decomposition the products mentioned above. The total yield of the oxidation products in this case is small and an amount of dark red resinous material is obtained from which nothing could be isolated. This method, therefore, is not found to be a promising one for the synthesis of the required sulpho-salicylic acid.



EXPERIMENTAL.

Quinoline-8-sulphonic acid and quinoline-5-sulphonic acid were prepared by the sulphonation of quinoline according to Riemer-Schmidt's method (*Ber.*, 1883, **16**, 721; *cf.* also Bedall and Fischer, *Ber.*, 1881, **14**, 443; 1882, **15**, 1979; Coste and Valeur, *Ber.*, 1887, **20**, 95). Since none of the authors give a precise quantitative data, the following details of the procedure will not only be found useful but more satisfactory for the isolation of the 5-acid.

Fuming H_2SO_4 (about 65% SO_3, 300 g.) was added in portions to quinoline (100 g.), and the mixture heated at 130°-140° for 1 hour. The cooled mixture was poured into water (800 c.c.) and, after standing for 12 hours, the separated quinoline-8-sulphonic acid was filtered off, washed and recrystallised from water (95 g.). A saturated solution of 50 g. of $HgCl_2$ was then added to the acid filtrate; the separated thick flocculent precipitate was filtered off, washed, dissolved in hot water and decomposed by H_2S. The filtrate from HgS was concentrated, when the 5-acid crystallises on cooling in the form of needles, yield about 30 g. The $HgCl_2$ forms a double compound crystallising from water in clusters of small needles. (Found: Hg, 42·15. $C_9H_7O_3NS, HgCl_2$ requires Hg, 41·66 per cent).

The above quinoline sulphonic acids (1 part) were reduced by pure tin (4 parts) and concentrated HCl (10 parts) (*cf.* Lellmann, *Ber.*, 1887, **20**, 3087; Claus, *J. pr. Chem.*, 1897, *ii*, **55**, 94). The quinoline-5-sulphonic acid, as obtained above, always contains some impurity of the 8-isomeride, which ordinarily cannot be easily separated. The method of reduction, however, forms an excellent method for the complete separation of the two acids. Thus the tetrahydro-8-acid (very light leaflets, m.p. 245°) is more insoluble in hot water, particularly in HCl solution than the corresponding 5-acid (thick stout needles, m.p. 315°-318°), and is thus easily removed.

Tetrahydroquinoline-8-sulphonic Acid.

Acetylation.—The finely powdered dry potassium salt was mixed with three times its weight of acetic anyhydride and the mixture gradually heated in an oil-bath at 135°-140°. The substance first dissolved (one hour) and was then immediately precipitated. The excess of anhydride was removed under reduced pressure (water-bath) and the solid washed with a mixture of absolute alcohol and dry ether; almost pure product was obtained, yield theoretical. It is very soluble in water, difficultly soluble in alcohol. Potassium acetyltetrahydroquinoline-8-sulphonate crystallises from water by slow evaporation in the form of thick long needles. (Found: K, 13·22; H_2O, 8·1. $C_{11}H_{12}O_4NSK, 1\frac{1}{2}H_2O$ requires K, 13·31; H_2O, 8·43 per cent. Found: S, 10·51. $C_{11}H_{12}O_4NSK$ requires S, 10·92 per cent).

Oxidation of the Acetyl Compound.—10 G. of the above K-salt (I) were dissolved in 200 c. c. of water and $KMnO_4$ (26 g., 5% solution) was gradually added in portions; the liquid soon became warm, each portion was added after the first was decolourised. When the whole was added (8 hours) the mixture was heated on the water-bath for about 15 minutes (excess $KMnO_4$ removed by alcohol) and filtered hot; the filtrate after nearly neutralising with dilute H_2SO_4 was concentrated and the separated K_2SO_4 removed, until some organic substance began to separate along with it. The concentrated liquid was acidified with dilute HCl when short needles separated; a further quantity was obtained from the mother liquor on concentration, yield about 7·2 g. (II). The freshly crystallised substance partly effloresces in air. The air-dried substance was analysed. [Found: S, 8·07; H_2O (at 130°) 2·3. $C_{11}H_7O_9NSK_2, \frac{1}{2}H_2O$ requires S, 7·86; H_2O, 2·16 per cent. Found: K, 18·69; Equiv., 405·7. $C_{11}H_7O_9NSK_2$ requires K, 19·16 per cent. Equiv., 407.] From the final mother liquor on concentration a small quantity of a substance (III) crystallising in clusters of small needles was obtained. [Found: H_2O (at 130°), 6·7. $C_{11}H_8O_9NSK, 1\frac{1}{2}H_2O$ requires H_2O, 6·81 per cent. Found: S, 8·99; Equiv., 185·1. $C_{11}H_8O_9NSK$ requires S, 8·67 per cent. Equiv., 184·5.]

6 G. of the substance (II) were heated to boiling for half an hour with HCl solution (1:2), the solution turning pale brownish red. The products obtained are KCl, some undecomposed substance and a substance (IV, 1 g.), which crystallises from water in cauliflower-like crystals. (Found: H_2O, 7·59. $C_9H_6O_8NSK, 1\frac{1}{2}H_2O$ requires H_2O, 7·62 per cent. Found: K, 12·02; Equiv., 163. $C_9H_6O_8NSK$ requires K, 11·92 per cent. Equiv., 163·5).

When substance (II) or (IV) was heated with concentrated HCl instead of dilute solution, the substance decomposed completely giving a dark bluish solution; the separated KCl was removed and the acid liquid was allowed to evaporate spontaneously when thick plates were obtained.

This crystallises from water in thick stout long needles which burn away without charring, leaving a white residue. It also reduces acidified $KMnO_4$ solution. It is, therefore, potassium tetraoxalate. (Found : Equiv., 84·79. $C_4H_3O_8K$, 2 H_2O requires Equiv., 84·66).

The coloured liquid on dilution gives a blue fluorescence, but no substance could be recovered from it.

Tetrahydroquinoline-5-sulphonic Acid.

Acetylation.—The powdered K-salt was mixed with 1½ times its wt. of acetic anhydride ; good deal of heat was evolved in this case, the substance almost dissolved and then immediately separated out. The mixture was heated at 135°-140° for 1 hour. It was worked up in the same way as the corresponding 8-derivative. Potassium acetyltetrahydroquinoline-5-sulphonate crystallises from water in thick plates, yield theoretical. (Found : S, 10·59 ; H_2O, 6·18. $C_{11}H_{12}O_4NSK$, 1 H_2O requires S, 10·92 ; H_2O, 5·7 per cent. Found : K, 13·12. $C_{11}H_{12}O_4$ NSK requires K, 13·31 per cent).

Oxidation of the Acetyl Compound.—27 G. of the above K-salt (V) in 550 c. c. of water were gradually treated in the cold with a 5% solution of 70 g. of $KMnO_4$ over a period of 8 days. The solution was filtered without warming and the faintly yellowish filtrate was almost neutralised by dilute H_2SO_4 ; K_2SO_4 was removed by gradual concentration on a water-bath ; finally the non-acidified concentrated liquid gave stout short white needles (7 g.) of a neutral substance containing potassium (VI). This was recrystallised three times from water and analysed. (Found : K, 21·62 ;H_2O, 6·65. $C_{10}H_7O_7NSK_2$, 1½ H_2O requires K, 21·48 ; H_2O, 6·92 per cent. Found: S, 9·13. $C_{10}H_7O_7$ NSK_2 requires S, 8·81 per cent).

The mother liquor was concentrated over solid NaOH in a vacuum desiccator when, along with a further small quantity of the substance (VI), a greyish white powder was obtained (0·7 g.), which crystallises from water in microscopic silky needles (VIII) ; slightly soluble in cold, but easily in hot water. It is an acid potassium salt and does not give the isatin compound on treatment with concentrated HCl. It gives, however, an *iso*cyanide reaction. It was twice recrystallised and analysed. (Found : S, 11·16 ; Equiv., 297·8. $C_9H_8O_6NSK$ requires S, 10·77 per cent. Equiv., 297. Found : H_2O, 6·25. $C_9H_8O_6$ NSK, 1H_2O requires H_2O, 5·71 per cent.) The substance, therefore, is an acid potassium salt of 2-acetylamino-6-sulphobenzoic acid.

The final mother liquor, a reddish liquid, was evaporated to dryness on a water-bath. The reddish yellow sticky mass (about 20 g.) was treated in the cold with concentrated HCl when a pulpy mass separated; when recrystallised from water, short needles were obtained (about 0·2 g.) which do not give the isatin compound with HCl. It is also found to be an acid potassium salt and gives the *iso*cyanide reaction. (Found: H_2O, 7·11. $C_7H_6O_5NSK, H_2O$ requires H_2O, 6·60 per cent. Found: Equiv., 255·2. $C_7H_6O_5NSK$ requires Equiv., 255.) The substance, therefore, appears to be an acid potassium salt of 2-amino-6-sulphobenzoic acid.

The filtrate from the above was warmed when a small quantity of isatin sulphonic acid (K-salt) was obtained, some KCl and potassium tetraoxalate were also recovered. The rest was a brownresinous mass from which nothing could be isolated.

The substance (VI) is a dipotassium salt of 2-acetylamino-6-sulphobenzoylformic acid. When warmed with a strong solution of HCl, it was decomposed with the liberation of acetic acid yielding a granular yellowish substance on cooling. This was removed, washed and recrystallised twice from water as yellow short silky needles. It is a potassium salt of isatin-4-sulphonic acid (VII) since it gives indophenin reaction. It is moderately soluble in cold but easily in hot water, sparingly soluble in alcohol. The freshly recrystallised substance, if allowed to stand in contact with its mother liquor for a few days, changes into beautiful ruby-red prisms with no water of crystallisation. (Found: S, 12·38; K, 14·61. $C_8H_4O_5NSK$ requires S, 12·07; K, 14·71 per cent).

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On Activated Charcoal. Part II. Purification by Washing with Water and by Activation.

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It has been reported by Roychoudhury (*J. Indian Chem. Soc.*, 1931, **8**, 433) and Roychoudhury and Mukherjee (*Z. physikal. Chem.*, 1931, **157**, 435) that the negative charge of the sugar charcoal diminishes on repeated washing with pure water and ultimately becomes positive on further activation. The conclusion was drawn that the primarily adsorbed layer of ions on the surface of charcoal determines it's property, such as, the adsorption of acids or alkalis and the liberation of alkali or acid by neutral salt solution.

Kolthoff (*J. Amer. Chem. Soc.*, 1932, **54**, 4473) found that charcoal activated at 900—1000° and heated, thereafter, in oxygen at 300°-500° forms on its surface a definite chemical compound with an acid character. The optimum temperature for preparing this acid charcoal is 400°. He also found that a suspension of $C_{400}°$ in water was negatively charged while a similar suspension of $C_{950}°$ in water was positively charged. Also, if $C_{950}°$ be shaken with an inorganic salt solution, hydrolytic adsorption of the acid takes place and the filtrate has an alkaline reaction. If on the other hand, $C_{480}°$ be shaken with an inorganic salt solution, the filtrate has an acid reaction. These observations are in agreement with those of Roychoudhury and Mukherjee (*loc. cit.*).

Miller (*J. Phys. Chem.*, 1932, **36**, 2967) objects to the procedure employed by Roychoudhury (*loc. cit.*) for heating the charcoal for activation at 600°, which, according to Miller, is not high enough to drive off the acid products on the charcoal surface. But Kolthoff (*loc. cit.*) states "by heating $C_{400}°$ for 24 hours in a vacuum at 620° it assumes the properties of $C_{950}°$. The acid has been removed from the surface and it adsorbs inorganic and organic acids almost to the same extent as $C_{500}°$."

Miller (*loc. cit.*) also states that the washing with boiling pure water followed by activation is not sufficient for the purification, as quantities of acids can be irreversibly adsorbed on the charcoal leaving no detectable amount of acid in solution.

Miller, however, finds that "at boiling temperature there was an appreciable quantity of acid extracted in solution." Roychoudhury (*loc. cit.*) had, however, decanted off the hot supernatant liquid and determined its specific conductivity, when it was sufficiently cold and the supernatant liquid was not allowed to become cold in contact with the charcoal.

It seems that Miller's objections to the procedures are based on misconceptions. Further, the object of the work of Roychoudhury and Mukherjee was to investigate the relationship between the surface charge and the adsorption of acids and bases or their liberation with neutral salts, and the charcoals with acidic surface layers were of as much interest as those without it.

Ockrent (*J. Chem. Soc.*, 1934, 301) holds that the oxide theory of the composition of the surface layer of activated charcoal is fallacious and that the differences in the adsorptive properties of charcoal, activated at different temperatures, are associated with the existence or absence of the high temperature adsorbed water layer. If the contentions of Ockrent be correct then the arrangement of Miller in removing surface oxides appears to be invalidated.

Further experiments have been carried out to ascertain the extent of purification which can be effected by the same procedure (Roychoudhury, *loc. cit.*). The samples of charcoals were also prepared in the same way.

RESULTS.

Effect of Washing and Activation.

Table I shows the results of washing directly after ignition of a sample of negative charcoal (A). 50 G. of charcoal were boiled with a litre of conductivity water for 1½ hours. Different stages of washing and activation at which the negative charge of sample A becomes zero have been indicated in the table by A_1, A_2 and A_3. The electro-osmotic movement of the bubble is given in cm. per 3 minutes at 36°-38° (Roychoudhury, *loc. cit.*), the proportion of charcoal and water being the same as used in the washing and the time of contact of charcoal and water being either 2 hours or 24 hours as indicated below.

TABLE I.

Sample.	No. of washings (1½ hr. boiling).	Sp. conductivity of		Rate of electro-osmosis (contact for 2 hrs).
		water used $\times 10^6$ (35°).	supernat. liquid $\times 10^6$ (35°).	
A	1	2·2	6·8	
	2	,,	4·4	
	3	,,	4·6	
	4	,,	2·9	
	5	1·7	2·2	
	6	2·2	2·9	
	7	,,	2·7	—24·1
	8	1·7	2·4	
	9	1·9	1·9	—15·1
	10	1·4	2·2	
	11	2·2	2·0	
A_1 (activated for 6 hours at 800°)	12	1·7	2·0	0*
	13	1·4	4·4	
	14	,,	3·7	
	15	,,	3·1	
A_2 (activated for 6 hours at 800°)	16	1·7	2·2	0*
	17	1·4	6·3	
	18	2·2	5·5	
	19	,,	4·9	
A_3 (activated for 6 hours at 800°)	20	,,	4·4	0*

Table II gives the results for another sample, B. At the third washing the charge was measured and the electro-osmotic movement of the bubble was found to be −11·0 cm. in 3 minutes. After the 13th washing the charcoal was activated (B_1), which was activated without further boiling with water (B_2). This process of activation without boiling with water was continued until B_4 was obtained.

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* No variation of charge even after 24 hours' contact.

TABLE II.

Sample.	No. of washings (15 min. boiling, 250 c.c. water + 50 g. of charcoal).	Specific conductivity of		Rate of electro-osmosis (contact for 2 hours).
		water used × 10^6 (35°).	supernat. liquid × 10^6 (35°).	
B	1	2·0	8·0	
	2	,,	7·0	
	3	,,	8·0	−11·0
	4	,,	6·5	
	5	,,	6·0	
	6	,,	6·5	
	7	,,	5·0	
	8	,,	3·8	
	9	,,	3·9	
	10	,,	3·7	
	11	,,	3·7	
	12	,,	2.5	
B_1 (activated for 6 hrs. at 800°)	13	,,	3·6	−11·3
B_2 (activated for 6 hrs. at 800°)	...	...	...	−0·2
B_3 (activated for 6 hrs. at 800°)	...	...	...	0
B_4 (activated for 6 hrs. at 800°)	...	...	...	0

It will be seen that the procedure of purification always leads to the promotion of charcoal with a discharged surface (iso-electric or null charcoal) and that on activation electrolytes are liberated from the surface which increases the specific conductivity of the washing water.

A portion of A was next treated with concentrated HCl before washing with conductivity water. The resulting charcoal C was then treated in a similar manner. The data are given in Table III.

TABLE III.

Sample.	Boiled for 1½ hrs. + 50 g. charcoal.	Specific conductivity of water used × 10^6 (35°).	Specific conductivity of supernat. liquid × 10^6 (35°).	Rate of electro-osmosis.
C	1	1·9	7·4	−13
	2	2·2	4·9	
	3	,,	21	
	4	,,	,,	
	5	1·4	22	−27·4
	6	2·9	,,	
	7	,,	24	
	8	,,	22	
	9	,,	19	
	10	,,	,,	
	11	2·2	14·8	
C_1 (activated for 6 hrs. at 800°)	12	2·3	,,	−2·9
	13	1·2	185	
	14	1·5	66	
	15	1·4	44	
	16	,,	,,	
	17	2·1	29	
	18	1·7	24	
	19	2·2	20	
	20	1·4	,,	
C_2 (activated for 6 hrs. at 800°)	21	,,	17	−3·0
	22	2·2	22	
	23	,,	21	
	24	1·4	22	
	25	,,	17	
	26	,,	,,	
	27	2·2	21	
	28	,,	19	
	29	1·7	17	
C_3 (activated for 6 hrs. at 800°)	30	,,	,,	0
	31	,,	22	
	32	,,	21	
	33	,,	17	
	34	,,	,,	
	35	1·4	15	
C_4 (activated for 6 hrs. at 800°)	36	,,	,,	0

Apparently it is difficult to remove the last traces of hydrochloric acid and activation was not sufficient to remove the last traces of the acid at the pressure of 10 mm. at which the activation was carried out, though the surface has already become neutral after the activation.

The surface charge of various samples of activated charcoal in contact with water is given in Table IV. The time of contact of the charcoal with water was 2 hours in each case. For the sake of comparison, some of them were also left in contact with the water inside the endosmotic tube for 24 hours. A_4 has been obtained after activating A_3 for 6 hours at 550°. B_5 was obtained from B_4 after activation at 550° in a new silica tube and B_6 was obtained from B_5 on further activation. D_1 is an unactivated coarse negatively charged sugar charcoal which on activation at 550° for 8 hours gave D_2; E is a sample of sugar charcoal positively charged; F_1 is also a sample of sugar charcoal not washed before activation and on first activation gave F_2, which on further activation gave F_3.

TABLE IV.

Activated sample.	No. of washings.	Temp. of activation.	Time of heating.	Rates of electro-osmosis.
A_1	20	800°	6 hrs.	0
A_2	...	,,	,,	0
A_3	...	,,	,,	0
A_4	...	550°	,,	0
B_1	...	800°	,,	−11·3
B_2	...	,,	8	−0·2
B_3	...	850°	,,	0
B_4	...	,,	6	0
B_5	...	550°	,,	0
B_3	...	850	,,	0
C_1	12	800°	6 hrs.	−2·9
C_2	...	,,	,,	−3·0
C_3	30	,,	,,	0
C_4	36	,,	,,	0
D_1	...	550°	8	−1·4
D_2	...	575° (in a new silica tube)	6	+0·8
E	...	550°	,,	+2·1
F_1	Not washed	,,	,,	−2·6
F_2	...	,,	,,	0
F_3	...	,,	,,	0

The negative charge invariably diminishes by continual washing and activation until the zero is reached. The negative charcoal could, however, be transformed into positive charcoal only in two instances (D_2 and E). In the case of D_2 the positive charge became zero after keeping the charcoal and water in contact for 24 hours. By the same treatment the positive charge of E decreased from 2·1 to 0·8 cm.

There is thus a general tendency for the specific conductivity of the supernatant liquid of charcoal to be decreased on successive washings which indicates that surface impurities are being gradually removed by this treatment. The fact that the negative charge of impure charcoal gradually decreases and becomes zero and then becomes positive shows that the removal of surface impurities plays a very important rôle in determining the surface charge of the charcoal. The positive charge in contact with pure water appears to be the best index of the purity of a charcoal surface. The difficulty in getting a positively charged surface lies in the removal of the last traces of electrolytic impurities. This explains why positively charged charcoals are not always produced under the conditions studied. Simply boiling the charcoal with conductivity water does not help much to decrease the negative charge unless the process of boiling is assisted by activation.

It has been contended by Miller that it is doubtful if all the acidic impurities can be removed by heating at 600°. It will be observed that positive charcoal can be obiained by heating the charcoal between 550° to 600° (D_2 and E).

Effect of Electrolytes on the Surface Charge.

The measurements were carried out at room temperature (27°-28°). 250 C.c. of the electrolytic solution were shaken with 15 g. of the charcoal. The time of contact was 24 hours.

TABLE V.

Sample A (negative).

	Movement of bubble in cm. per 3 minutes			
Conc.	HCl.	H_2SO_4	NaOH.	NaCl.
0	−12·05	−8·95	−9·8	−8·5
0·0001*N*	−11·65	−9·2	−13·9	−11·7
0·0002	−10·1	—	−18·1	−17·2

TABLE VI.

Sample A_3 (iso-electric).

Conc.	Movement of bubble in cm. per 3 minutes. HCl.	 H_2SO_4.
0	0	0
0·0001 *N*	−3·9	−6·8
0·0002	−7·0	−17·0
0·0004	−12·3	—
0·0005	−10·4	—

TABLE VII.

Sample D (positive).

Electro-osmotic experiments with positively charged sugar charcoal (vide Table VI).

Conc.	Movement of the bubble in cm per 3 minutes. HCl
0	+0·8
0·0001 *N*	0
0·0002	0
0·001	+4·0

For comparison the following data from Roychoudury (*loc. cit.*) is given.

TABLE VIII.

Experiments with positively charged sugar charcoal with the addition of electrolytes (From Roychoudhury, *J. Indian Chem. Soc.*, 1931, 8, 560).

Conc.	HCl.		H_2SO_4.	NaOH.
	Sample I.	Sample II.		
0	1·5	+1·3	+6·13	+0·9
0·0001*N*	−0·25	−0·35	−0·1	−0·25
0·0002	−0·25	−0·4	−0·45	−0·45
0·001	+1·0	+0·78	−3·0	−0·91

SUMMARY.

1. It appears that the charge of positively charged charcoal is least affected by the above electrolytes. It is difficult to prepare positively charged charcoal. The negative and iso-electric charcoals show a strong adsorption of anions.

2. The absorbed layer of electrolytes on the charcoal surface cannot alone be removed by long continued washing and it is necessary to activate the charcoal to remove them.

3. Hydrochloric acid is difficult to remove. If the charcoal has been purified by activation the charge is affected by hydrochloric acid only to a small extent.

We take this opportunity of expressing our thanks to Professor J. N. Mukherjee for suggesting this work and for facilities.

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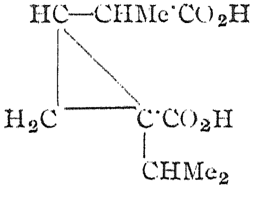
A Synthesis of *cis*-and *trans-dl*-1-*iso*Propyl*cyclo*propane-1:2-dicarboxylic Acid and Experiments towards the Resolution of the *cis-dl*-Acid.*

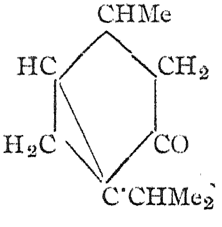
By S. K. Ranganathan.

Direct evidence for the presence of *cyclo*propane ring in the various acids derived from thujane series of compounds has not been furnished so far. The object of the present investigation was to furnish such an evidence by synthesising the simplest member of this group of acids, *viz.* umbellularic acid.

Tutin (*J. Chem. Soc.*, 1906, **89**, 1104; 1908, **93**, 252) found that umbellulone, on oxidation with permangante, gave rise to a ketonic acid, umbellulonic acid, which yielded a lactone on distillation. Umbellularic acid was obtained from this lactone by oxidation with permanganate and had m.p. 120-121° (with 1 H_2O, 85°); $[\alpha]_D = -89{\cdot}7°$ (in $CHCl_3$). Tutin excluded a *cyclo*propane ring structure for this acid on account of its marked stability to permanganate, hydrochloric and nitric acids and was inclined to regard it as 1-methyl-*cyclo*pentane-2:4-dicarboxylic acid. Semmler (*Ber.*, 1907, **40**, 5019; 1908, **41**, 3988), however, obtained by oxidising the benzylidene derivative of β-dihydroumbellulone, *d*-homothujadicarboxylic acid (I) which could only be the case if β-dihydroumbellulone and umbellulone were (II) and (III) respectively. From this it follows, that umbellulonic acid, the lactone and umbellularic acid are (IV), (V) and (VI) respectively.



(I)



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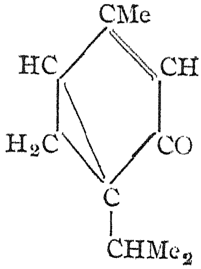

(III)

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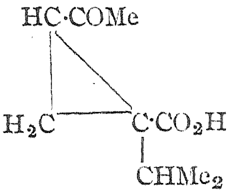
* A short note on the synthesis of the *dl*-acid is in course of publication in Nature. We had started work on resolution of our synthesised acid when Rydon's note (*Chem. Ind.*, 1936, **55**, 294) came to our notice and we have subsequently carried the resolution through. No details of Rydon's investigation have appeared till the date of writing this paper (21-5-1936).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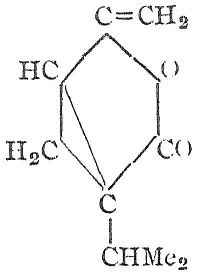
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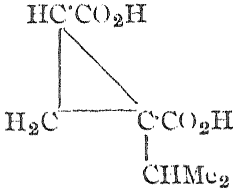
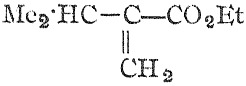

(VI)

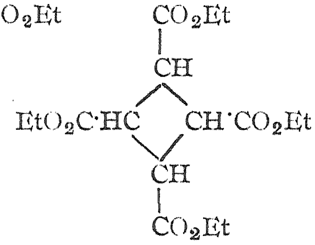
A ready method of synthesising the acid (VI) would be to treat ethyl γ-bromo-α-*iso*propylglutarate or ethyl α-bromo-α-*iso*propylglutarate with concentrated alkali (Ingold, *J. Chem. Soc.*, 1925, **127**, 387). The results of Hariharan, Menon and Simonsen (*J. Indian Inst. Sci.*, 1928, **11A**, 107) on the bromination of α-*iso*propylglutaric acid did not indicate this to be a promising line of attack. Adopting the method of Owen and Simonsen (*J. Chem. Soc.*, 1932, 1426; 1933, 1226) it was thought that ethyl α-*iso*propyl acrylate (VII) (Blaise and Luttringer, *Bull. Soc. chim.*, 1905, *iii*, **33**, 648, 776) would condense with ethyl diazoacetate in the presence of copper-bronze to yield in one stage the diethyl ester of (VI). Though there was smooth reaction at 35° between the above substances the product consisted mainly of ethyl *cyclo*butane-1:2:3:4-tetracarboxylate (VIII) (*cf.* Owen and Simonsen, *loc. cit.*), about 70% of the acrylic ester remaining unchanged. This result is not very surprising in view of the fact that the success of Owen and Simonsen (*loc. cit.*) was largely due to the presence of *gem*-dimethyl group taking part in the desired *cyclo*propane ring formation.

Following the method of Auwers and collaborators (*Annalen*, 1929, **470**, 284; 1932, **496**, 27, 252), ethyl α-*iso*propylacrylate was condensed with ethyl diazoacetate to give ethyl 5-*iso*propyl-$\triangle^1$-pyrazoline-3:5-dicarboxylate (IX) in good yield. On heating at 200°, the latter lost nitrogen yielding the mixed esters, b. p. 144-148°/28 mm. Hydrolysis of this gave *trans-dl-iso*propyl*cyclo*propane-1:2-dicarboxylic acid. The amount of *trans*-acid formed constituted about 35% of the hydrolysed product, the rest being a liquid mixture of unsaturated acids, the examination of which is as yet incomplete. The presence of α-*iso*propylglutaconic acid is to be expected in this mixture.

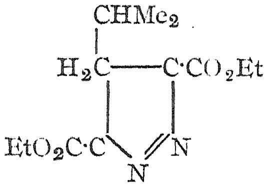


$Me_2{\cdot}HC-\underset{\underset{CH_2}{\|}}{C}-CO_2Et$

(VII)



(VIII)



(IX)

trans-dl-1-*iso*Propyl*cyclo*propane-1:2-dicarboxylic acid (m. p. 194-95°) was stable to permanganate and was converted to the anhydride of the *cis*-acid by heating with acetyl chloride at 180°. The *cis*-acid (m. p. 124-125°, with $1H_2O$, 93-95°) was in turn stable to permanganate and could be converted to its anhydride on heating at 150°. Concentrated hydrochloric acid at 180°, as also boiling nitric acid, had no action on it.

The resolution of the *dl-cis*-acid with a view to obtain Tutin's *l*-acid was undertaken first with brucine. The *d*-acid could be obtained in a fair state of optical purity. For obtaining the *l*-form, the acid was combined with cinchonidine, when the salt of the *l*-form proved more insoluble. Due to the smallness of material at disposal, the active acid, however, could not be obtained very pure.

EXPERIMENTAL.

Ethyl α-*bromo*iso*valerate* was prepared in 85% yield starting from *iso*valeric acid (Schleicher, *Annalen*, 1892, **267**, 120). It was not necessary to isolate the intermediate bromoacid-bromide. B. p. 88-90°/24 mm. ; d_4^{26}, 1·276; n_d^{26}, 1·4465 ; whence $[R_L]_D = 43{\cdot}71$; calc. 43·83.

Ethyl α-iso*propylhydracrylate* was prepared in 60% yield from the above and trioxymethylene (Blaise and Luttringer, *loc. cit.*), b. p. 115-18°/25 mm.; n_d^{26}, 1·4300 : d_4^{26}, 0·9863 ; whence $[R_L]_D = 41{\cdot}94$. Calc. 42·32.

Ethyl α-iso*propylacrylate* (VII) was prepared in about 55% yield by dehydrating the hydroxy ester with P_2O_5 (Blaise and Luttringer, *loc. cit.*), b. p. 147-149°/685 mm.

Condensation of Ethyl α-iso*propylacrylate with Ethyl diazoacetate*.—To a mixture of the substituted acrylic ester (12 g.) with copper bronze (0·5 g.), diazoacetic ester (9·6 g., b. p. 59°/25 mm. approx.) was added dropwise during the course of 3-4 hours, the temperature being maintained at 30-35°. The reaction was vigorous with evolution of nitrogen. After standing for some time, a fresh lot of the unsaturated ester (12 g.) was added and the diazo ester (9·6 g.) dropped as above. The experiment was repeated with another lot in the same flask with a fresh amount of catalyst (0·5 g.). After the addition was over, the temperature was cautiously raised to 50° and maintained at 50-60° for 3 hours. The catalyst was filtered off, and the product (50·4 g.) distilled, and the following fractions were collected : (i) 42-60°/5 mm, 21 g.; (ii) 95-105°/4 mm., 11·5 g. ; (iii) 105-120°/4 mm., 2·5 g. ; (iv) above 140°/4-10 mm., 1·5 g. with decomposition. Brownish black residue was left in the flask. Fractions (ii) and (iii) were mixed and redistilled: 3-4 g. distilled below 70°/2 mm. and the main fraction (9-10 g.) distilled at 85-100°/2 mm.

The main fraction was hydrolysed with methyl alcoholic potash (12%), when the potassium salt separated (2·5 g.). The acid isolated from the potassium salt melted at 274°, and was thus proved to be *cyclo*butane-1:2:3:4-tetracarboxylic acid (Owen and Simonsen, *loc. cit.*). From the alcoholic solution, after evaporation and acidification, 1·2 g. of a thick oil was obtained (b. p. 120-150°/26 mm.). The oil did not solidify on standing. It was unstable to neutral $KMnO_4$.

Ethyl 5-iso*propyl*-Δ^1-*pyrazoline*-3:5-*dicarboxylate* (IX).—The unsaturated ester (32·5 g.) was mixed with the diazo ester (24·5 g., 1 molecule each), in a three-necked flask fitted with reflux condenser and thermometer. There was no reaction in the cold. However, on warming the flask got heated up and when the temperature rose to 70°, it was cooled with water and the process of heating and cooling was repeated twice. Subsequently, the contents of the flask were maintained at 55° for 18 hours. The yellowish brown product was distilled, when the main fraction (33 g.) distilled constantly at 164°/4 mm. A small amount distilled at 45-60°/8 mm. and another fraction at 115-120°/6 mm. The main fraction was redistilled as a pale yellow viscous oil, b. p. 158°/1 mm. ; n_d^{30}, 1·4814. (Found : N, 10·73. $C_{12}H_{20}O_4N_2$ requires N, 10·94 per cent).

The pyrazoline ester immediately decolourises cold alkaline permanganate and absorbs bromine in $CHCl_3$. Attempt to isolate the pyrazole derivative was not successful. The ester (5 g.) was dissolved in $CHCl_3$ (15 c. c.) and bromine (1·2 c. c. in 10 c. c. of $CHCl_3$) was added drop by drop, decolourisation occurred with evolution of HBr. After standing for 24 hours, the chloroform was removed under diminished pressure and the residue distilled in vacuum when decomposition occurred; main fraction 120-125°/2 mm. (ester was free from nitrogen).

Decomposition of the Pyrazoline Ester by Heat.—The ester was heated in 2 lots of 16 g. and 13 g. each at 200° for 1 hour when the product (15·2 g.) distilled at 148-155°/30 mm. (redistilled at 144-148°/28 mm.). The high boiling fraction (170-200°/30 mm.) was again heated at 200° for 1 hour and on distillation gave 7·5 g. at 148-152°/30 mm, total yield 22·7 g. The ester, though unstable towards cold alkaline or neutral permanganate, does not take up bromine in CS_2 or $CHCl_3$.

trans-dl-1-iso*Propyl*-cyclo*propane*-1 : 2-*dicarboxylic Acid* (VI).—The above ester (22·7 g.) was mixed with methyl alcohol (80 c. c.), water (17 c. c.) and KOH (17 g.) and refluxed on the water-bath for 1 hour. The alcohol was then evaporated off, the residue dissolved in water, acidified with sulphuric acid and repeatedly extracted with ether (6 times). After removing ether the residue partly solidified. It was distilled in steam for 15 minutes and the residue allowed to cool when the *trans*- acid crystallised out, yield 6 g. The yield of the *trans*-acid was not improved by using platinum as catalyst during pyrolysis of the ester (Kohler and Steele, *J. Amer. Chem. Soc.*, 1919, **41**, 1093). The mother liquors yielded a thick viscous oil, unstable to permanganate and distilling at 140-170°/4 mm. (8·5 g.).

The *trans*-acid when recrystallised from water separated in glistening rectangular prisms, m. p. 194-95°. A search for the *cis*-acid in the mother liquor did not meet with success (*cf.* Verkade, *Rec. trav. chim.*, 1922, **41**, 208). It is easily soluble in alcohol, ether, acetone, difficultly soluble in $CHCl_3$, benzene and water. Prolonged boiling with alkaline permanganate effected little change. [Found: C, 56·13; H, 7·20; Equiv., 86; M. W. (Rast), 185·1. $C_8H_{12}O_4$ requires C, 55·82; H, 6·98 per cent. Equiv., 86; M.W., 172. Found: Ag, 54·95. $C_8H_{10}O_4Ag_2$ requires Ag, 55·9 per cent].

cis - dl - 1 - iso*Propyl*cyclo*propane*-1 : 2-*dicarboxylic Acid.*—The *trans*-acid (2 g.) was heated with acetyl chloride (5 c. c.) in a sealed tube for 3 hours at 180°. The anhydride of the *cis*-acid distilled at

140°/20 mm. (approx.) and at 113°/4 mm. It was a liquid which did not solidify (Tutin gives b. p. 167-69°/50 mm. for umbellularic anhydride). (Found : C, 62·03 ; H, 6·77. $C_8H_{10}O_3$ requires C, 62·33; H, 6·49 per cent).

The *cis*-anhydride dissolved in boiling water and the solution on cooling deposited the *cis*-acid. When crystallised from water the acid separated in prisms with 1 molecule of H_2O, which melted at 95° (sintering at about 85° ; complete fusion does not take place over a large range). (Found : C, 50·48 ; H, 7·81 ; H_2O, 9·97 ; Equiv, 94·3. $C_8H_{12}O_4$, H_2O requires C, 50·52 ; H, 7·41 ; H_2O, 9·47 per cent. Equiv., 95).

The anhydrous *cis*-acid obtained from an ethereal solution crystallises in plates from benzene-petroleum ether, m. p. 124-25° (shrinking at 121°). The acid is easily soluble in alcohol, ether, $CHCl_3$, CCl_4, moderately soluble in benzene and water. (Found : C, 56·1 ; H, 6·90 ; Equiv., 85·86. $C_8H_{12}O_4$ requires C, 55·82 ; H, 6·98 per cent. Equiv., 86).

The *cis*-acid on heating at 150° for 15 minutes loses water and goes over to its anhydride. It is stable to boiling alkaline permangnate. The *cis*-acid (0·1 g.) was heated with concentrated HCl (1 c. c.) at 180-190° for 3 hours (sealed tube). From the contents of the tube on opening, the *cis*-acid was isolated, m. p. 93°. Similarly it was isolated unchanged after heating with 8 times its weight of HNO_3 (3 parts of acid to 1 of H_2O) for 5 hours.

p-*Toluil of* cis-*Acid*.—The anhydride, obtained from 0·1 g. of the *cis*-acid by heating at 150°, was heated with *p*-toluidine (0·15 g.) for 5 minutes, the product treated with water and the *p*-toluil crystallised from dilute alcohol in needles, m. p. 89°. (Found : N, 6·35. $C_{15}H_{17}O_2N$ requires N, 5·76 per cent).

Resolution of the cis-dl-*Acid with Brucine*.—The *cis*-acid containing 1 molecule of water of crystallisation (3·25 g., 1 mol) was mixed with brucine (13·5 g., 2 mols; m.p. 178°) and dissolved in 230 c.c. of boiling water, filtered hot and allowed to cool; 6·1 g. of salt separated after a few hours. This was recrystallised from water 3 times. It gave $[\alpha]_D^{80} = -25{\cdot}63°$. It crystallised in plates from water, began losing water at 95° and melted at about 108°. [Found: N, 4·97; H_2O (at 130°), 14·5. $C_{54}H_{64}O_{12}N_4$, $9H_2O$ requires N, 4·99 ; H_2O, 14·1 per cent).

The free active acid was obtained by decomposing the above salt in the usual way. It crystallised in prisms from benzene. It gave $[\alpha]_D^{32} = +82{\cdot}42$.

Since, however, the acid was not optically quite pure, it was again combined with brucine, the brucine salt was recrystallised and the acid liberated again, $[\alpha]_D^{31}$, $+87{\cdot}7$.

The acid melted at 118° (prisms from benzene). It was obtained in thick needles by slow evaporation from water, m.p. about 83° (complete fusion not taking place). (Found : C, 55·91 ; H, 7·16. $C_8H_{12}O_4$ requires C, 55·82, H, 6·38 per cent). From the mother liquors it was not found possible to isolate the *l*-acid with specific rotation greater than $-66{\cdot}6°$.

Resolution of the cis-dl-*acid with Cinchonidine.*—The solution obtained from the *cis*-acid (1 mole, 2·4 g. containing $1H_2O$) and cinchonidine (1 mole, 3·7 g.) by boiling with 800 c.c. of water, was filtered, since no salt separated during 7 hours' standing it was concentrated to 300 c.c. when 4 g. of salt were deposited. This was recrystallised from water four times when 0·3 g. of salt was obtained as needles, m.p. 191° (decomp.). (Found: N, 5·92. $C_{19}H_{22}N_2O{\cdot}C_8H_{12}O_4$ requires N, 6·00 per cent). The salt being very sparingly soluble in the usual solvents its rotation could not be taken.

The above salt was decomposed in the usual way and the active acid was obtained by extracting with ether. It showed $[\alpha]_D^{31} = -81{\cdot}13°$.

As the *l*-acid was not optically pure, the melting point of the acid (prisms from benzene) was rather low and was 114°.

The author's grateful thanks are due to Prof. P. C. Guha for his kind encouragement and keen interest, and to the Government of Madras for a scholarship.

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On the Fluorination of Organic Compounds. Part II.

By P. C. Rây and Anil Chandra Ray.

In continuation of our work (Rây, Goswami and Ray, *J. Indian Chem. Soc.*, 1935, **12**, 93) we have attempted to prepare organic fluo-compounds by the action of thallous fluoride on aliphatic and aromatic compounds containing a reactive halogen atom. By following this method we have obtained methyl and ethyl fluoacetates as also benzyl fluoride. In other cases, either the products could not be isolated in pure condition or the reaction products decomposed. Thallous fluoride did not, however, react with α-bromoacetoacetic ester, α-bromopropionic ester, α-bromocinnamic acid, bromo*cyclo*hexane, chloroacetamide, iodoacetaldehyde, bromocamphor, *m*-bromonitrobenzene, under the experimental conditions described below. Hence this method of fluorination is not of so wide an applicability as was supposed by us. The above three fluo-compounds had the properties ascribed to them by Swarts (*Bull Soc. chim.*, 1896, *iii*, **15**, 1134) and by Ingold and Ingold (*J. Chem. Soc.*, 1928, 2249). Our method for the preparation of benzyl fluoride is easier than that of Ingold and Ingold. The yield is also better.

EXPERIMENTAL.

Methyl Fluoacetate.—Methyl bromoacetate (16 g.), anhydrous thallous fluoride (24 g.) and absolute alcohol were refluxed together for 36 hours. The reaction mixture was then filtered and the filtrate was kept in contact with anhydrous calcium chloride. The liquid was then fractionated. On redistillation, methyl fluoacetate was obtained as a colourless liquid, slightly lachrymatory, soluble in water, b.p. 104°. (Found : F, 20·00. Calc. for $C_3H_5O_2F$: F, 20·65 per cent).

Ethyl Fluoacetate.—Ethyl bromoacetate (24 g.), anhydrous thallous fluoride (40 g.) and absolute alcohol were refluxed together for 24 hours. The filtrate from the reaction mixture was fractionated, when a colourless liquid, b. p. 126°, was obtained. (Found : F, 17·1. Calc. for $C_4H_7O_2F$: F, 17·9 per cent).

Benzyl Fluoride.—An alcoholic solution of benzyl bromide (18g.) was reluxed with anhydrous thallous fluoride (30 g.) for 32 hours. The filtrate of the reaction product was freed from alcohol on the water-bath and the residue distilled, when a light yellow viscous distillate was obtained, b.p. 140°. It is lachrymatory and decomposes slowly evolving hydrofluoric acid (Found : F, 17·00. Calc. for C_7H_7F : F, 17·27 per cent).

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Variation of Cataphoretic Velocity of Colloidal Particles during Aggregation. Part II.

BY JNANENDRA NATH MUKHERJEE, SUBODH GOBINDA CHAUDHURY AND JYOTIRMOY SEN-GUPTA.

In a recent paper (Mukherjee, Chaudhury and Bhabak, *J. Indian Chem. Soc.*, 1936, **13**, 370) it has been shown that for a number of colloids and electrolytes

(*i*) the cataphoretic velocity increases with time with progressing aggregation of the colloidal particles at a constant concentration of the added electrolyte;

(*ii*) the increase in c. v. with time is often more marked, the higher the valency of the precipitating ions;

(*iii*) the c.v. of the supernatant suspension of a colloid after partial coagulation is less than that of the colloid before coagulation;

(*iiii*) the c.v. of the coagula of a sol (As_2S_3) is the same as that of the supernatant suspension of the colloid after coagulation.

These results are contradictory to the existing theories (Mukherjee, Chaudhury and Bhabak, *loc. cit.*), which lay the main stress on the thickness and the capacity of the double layer, on the radius of the particle and on the ionic strength of the medium and neglect the changes in the distribution of ions on aggregation which appear to be more important than the factors just mentioned. An explanation on this basis has been put forward by Mukherjee, Chaudhury and Ghosh (*Trans. National Inst. Sci. India*, 1936, **1**, 47-82) and by Mukherjee, Chaudhnry and Bhabak (*loc. cit.*). Further information is desirable on several points. In the present paper these observations have been extended to a wider range of concentrations of electrolytes and several other colloids. Some of the previous experiments have been confirmed.

EXPERIMENTAL.

Preparation of the Colloids.

Arsenious Sulphide.—25 C.c. of a saturated solution of As_2O_3 in distilled water were diluted with an equal volume of water and then mixed up with 500 c.c. of water saturated with hydrogen sulphide. Hydrogen sulphide washed through water was then passed till there was no further change in colour. Hydrogen gas was then bubbled through the solution to free it from excess of H_2S.

Vanadium Pentoxide.—About 10 g. of ammonium vanadate was triturated in a mortar with a few drops of strong hydrochloric acid till the mass was converted into a deep red paste. This was washed with several changes of water till the mass began to peptise. It was then shaken up with a large volume of water resulting in a dark red stable sol (sp. condty., 5×10^{-4} mho.).

Selenium Hydrosol.—H_2SeO_3 was added in minute quantities to about 3 c.c. of $NH_2 \cdot NH_2 \cdot H_2O$ and the precipitated Se was peptised by shaking. The resultant dark red solution was diluted till no appreciable opalescence appeared (sp. condty., 7×10^{-4} mho.).

Uranyl Ferrocyanide.—Equal volumes of 0·1 N-$UO_2(NO_3)_2$, $6H_2O$ and $K_4Fe(CN)_6$, $3H_2O$ were mixed together and the resulting precipitate washed by centrifuging with conductivity water till a stable sol was obtained. The larger particles were removed by centrifuging the sol (sp. condty., 5×10^{-5} mho.).

Copper Ferrocyanide.—It was prepared in the same way as uranyl ferrocyanide using (0·1N) solutions of $CuSO_4$, $5H_2O$ and $K_4Fe(CN)_6$. The larger particles were removed by centrifuging this sol (sp. condty., 3×10^{-4} mho.).

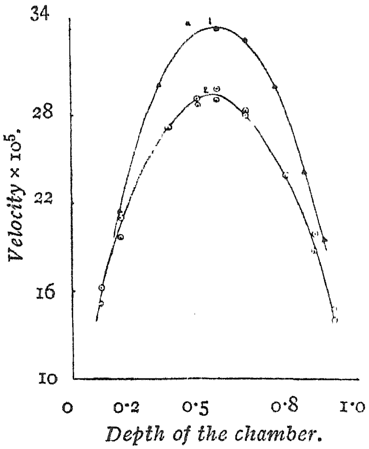
Hydrated Ferric Oxide.—To a litre of boiling conductivity water about 100 c. c. of an approximately 5% ferric chloride solution were added with stirring and the boiling continued for another 10-15 minutes. The sol was black in reflected light. It was then dialysed in a parchment bag for four days (sp. condty., 4×10^{-4} mho.).

The Parabolic Curve.

The cataphoretic velocities of particles at different depths of a cell when plotted against their respective depths should give a parabolic curve (Smoluchowski, Graetz, "Handbuch der Elektrizität u.d.

FIG. I.

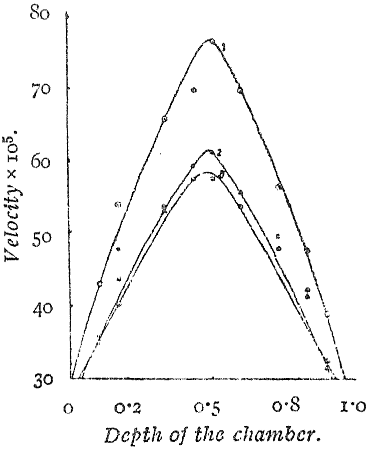
As_2S_3 *suspension.*



Curves 1 and 2 refer respectively to suspensions after coagulation with NaCl and $BaCl_2$.

FIG. 2.

V_2O_5 *sol.*



Curves 1-3 refer respectively to pure sol, $N/80$-KCl and $N/160$-KCl.

FIG. 3.

Uranyl ferrocyanide sol;

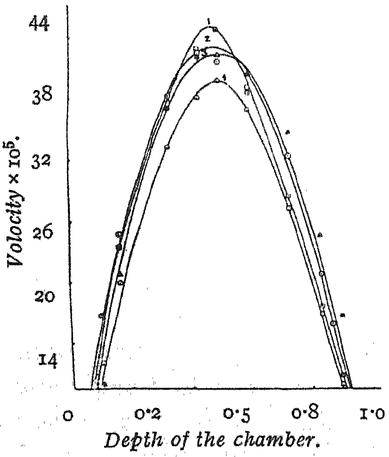
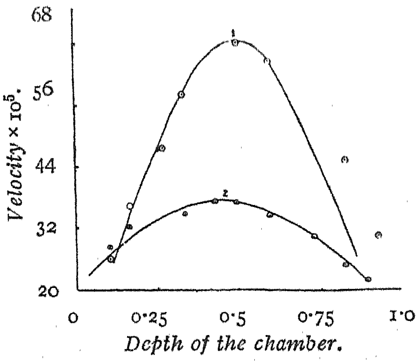


FIG. 4.

Se *sol and* $Fe(OH)_3$ *suspension.*

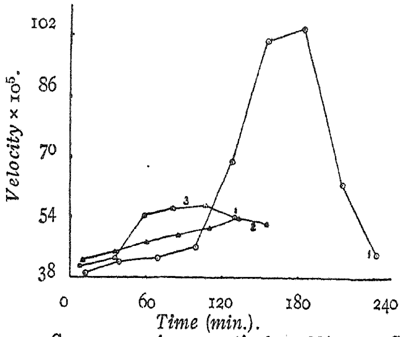


Curves 1-4 refer respectively to $N/1000$-KCl, pure sol, $N/800$- and $N/1500$-KCl.

Curve 1 refers to Se sol and curve 2 to hydrated Fe_2O_3 coagulated by K-oxalate.

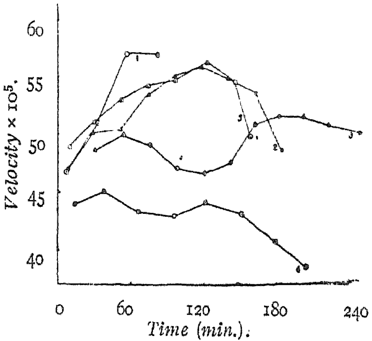
Magnetismus ", 1914, II, 2, p. 383). Observations were made with the pure sols excepting As_3S_3 and $Fe(OH)_3$, where in the pure sols, the particles were too small to be visible under the microscope and readings were taken after coagulation of this sol with solid NaCl (Fig. 1) or $N/300$-$BaCl_2$ (Fig. 1). The ferric oxide sol was also coagulated by ($N/525$) potassium oxalate (Fig. 4). The V_2O_5 and uranyl ferrocyanide sols were also mixed with equal volumes of such concentrations of KCl as would not cause any appreciable coagulation and therefore the c.v. should not vary during the interval of the experiment (Figs. 2 and 3 respectively).

FIG. 5.
As_2S_3 *sol.*



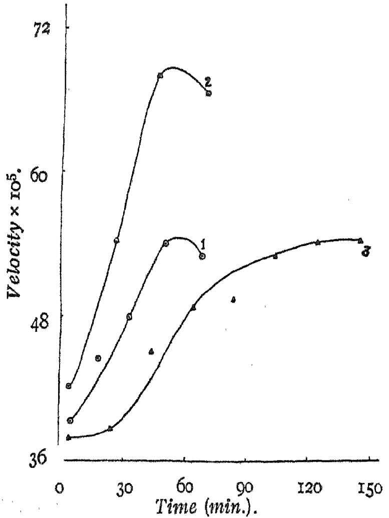
Curves 1-3 refer respectively to $N/25$-, $N/20$- and $N/16$-HCl.

FIG. 6.
As_2S_3 *sol.*



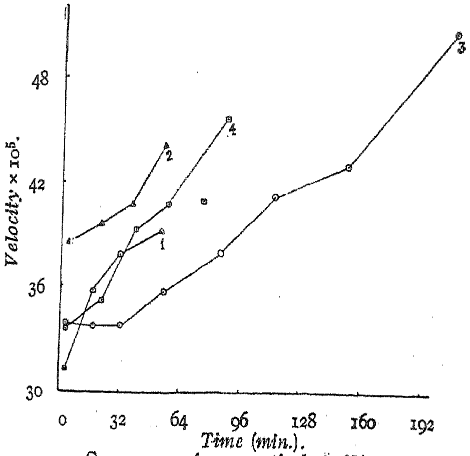
Curves 1-4 refer respectively to $N/5$-, $N/7$-, $N/8$- and $N/10$-NaCl and curve 5 to $N/8$-KCl.

FIG. 7.
V_2O_5 *sol.*



Curves 1-3 refer respectively to $N/40$-, $N/45$- and $N/50$-KCl.

FIG. 8.
V_2O_5 *sol.*



Curves 1-4 refer respectively to $N/1500$-, $N/1800$-, $N/2000$- and $N/2500$-$BaCl_2$.

From Figs. 1 to 8, it is found that with low concentrations of electrolytes such as would not produce any perceptible coagulation, the parabolic form of the curve required by Smoluchowski's theory is verified to an accuracy obtained by other authors (Abramsohn, *J. Gen. Physol.*, 1929, **12**, 711; *J. Phys. Chem.*, 1931, **35**, 331). The above results could be reproduced only when the cell is carefully cleansed. The c.v. values are found to be reproducible within ± 1%.

RESULTS.

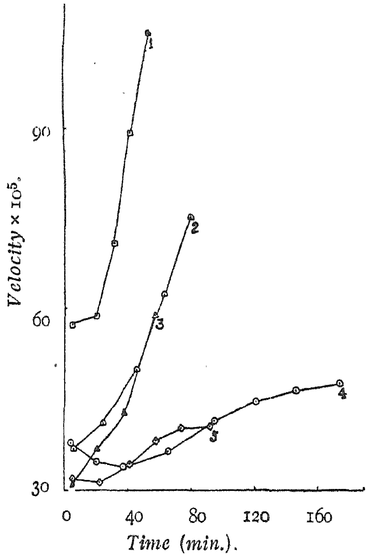
In the following are given the references to the figures, illustrating the effect of different electrolytes on the c.v. of various colloids with time.

No.	Sol.	Electrolytes used.	Figs. for reference
1	As_2S_3	KCl; NaCl; HCl	5 and 6
2	V_2O_5	KCl; $BaCl_2$; $AlCl_3$	7, 8 and 9
3	Se	Do	10, 11, 12.
4	$Cu_2Fe(CN)_6$	Do	13, 14.
5	$(UO_2)_2Fe(CN)_6$	KCl; $BaCl_2$	15
6	$Fe(OH)_3$	KCl; $BaCl_2$; K-oxalate, K-citrate	16
7	As_2S_3	KCl	17

In Figs. 13 and 15, the effect on c. v. of both peptisation and coagulation is given together. Equal volumes (100 c.c. each) of the precipitants (0·1*N*) were mixed together ($CuSO_4$, $5H_2O + K_4Fe(CN)_6$, $3H_2O$) in case of $Cu_2Fe(CN)_6$ and $UO_2(NO_3)_2$, $6H_2O + K_4Fe(CN)_6$, in case of $(UO_2)_2Fe(CN)_6$). The precipitate was washed by centrifuging, using 200 c. c. conductivity water each time till the precipitate peptised to give a stable sol. The c.v. was measured after each washing. After keeping for a few days, the c. v. was found to increase. A decrease was observed after centrifugalisation of the sol (*cf.* Chaudhury, *J. Indian Chem. Soc.*, 1933, **10**, 431). The centrifuged sol was taken and the c.v. noted with time as usual after adding different electrolytes mentioned above.

FIG. 9.

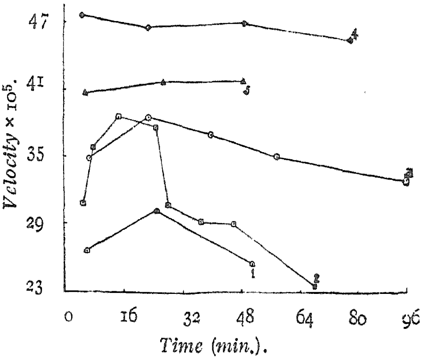
V_2O_5 *sol.*



Curves 1-5 refer respectively to *N*/5000-, *N*/6000-, *N*/6500-, *N*/7000- and *N*/10000-$AlCl_3$.

FIG. 10.

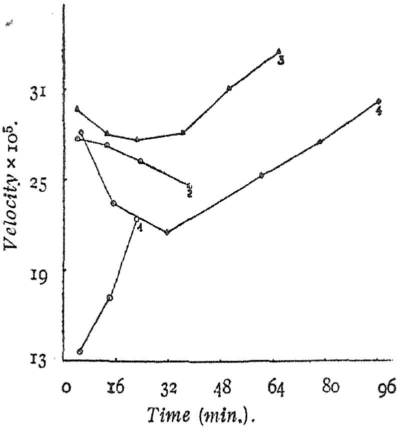
Se *sol.*



Curves 1-5 refer respectively to *N*/2-, *N*/5-, *N*/8-, *N*/10-, and *N*/20- KCl.

FIG. 11.

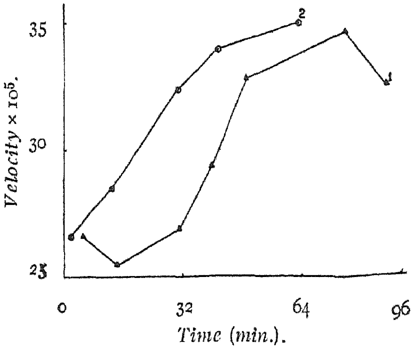
Se *sol.*



Curves 1-4 refer respectively to *N*/20-, *N*/50-, *N*/100-, and *N*/500-$BaCl_2$.

FIG. 12.

Se *sol.*



Curves 1 and 2 refer respectively to *N*/1000- and *N*/1200- $AlCl_3$.

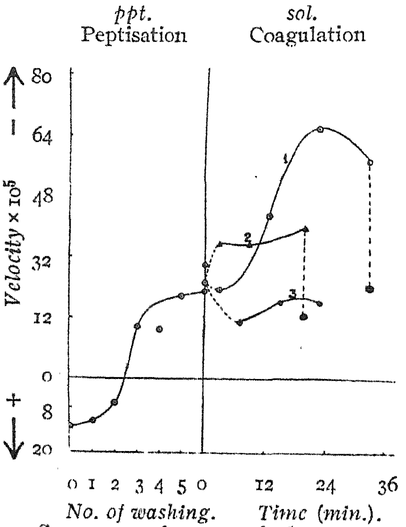
An analysis of the results obtained shows that the c.v. of a colloid always increases with time in presence of coagulating concentrations of electrolytes (Mukherjee, Chaudhury and Bhabak, *loc. cit.*) and when the time of observation is prolonged, a decrease in the c. v.

is observed. Moreover, another characteristic, quite often observed with the colloids and electrolytes so far studied, is that for higher concentrations of an electrolyte, the percentage increase in the c. v. observed with time is always larger. At low concentrations of electrolytes, irregular variations in the c. v. have been observed. Thus with arsenious sulphide sol and 0·04*N*-HCl there is observed an abnormal increase in c. v. after 2 hours of the mixing of the colloid and the electrolyte, followed by a sharp decrease. In the presence of 0·12*N*-NaCl, the variations in the c. v. of a colloid are also irregular, (*cf*. Figs. 5 and 6).

Vanadium Pentoxide Sol.—Curve 2, Fig. 7 and curve 4, Fig. 8 are exceptions to the concentration effect, *i.e.*, the greater the concentration taken, the larger the percentage of increment in c. v. with time. The concentration effect is clearly evident with V_2O_5 hydrosol and $AlCl_3$ (Fig. 9). Comparing Figs. 7, 8 and 9, it would appear that there is a valency effect, *i.e.*, the higher the valency of the precipitating ion, the larger the percentage increase in c. v.

FIG. 13.

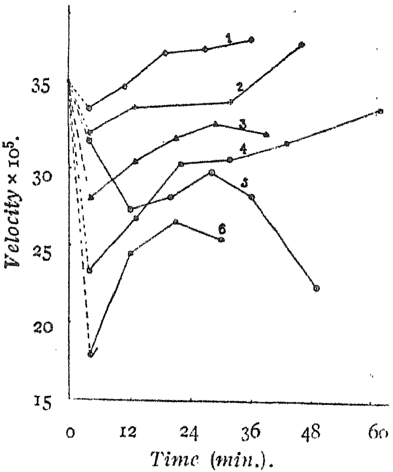
$Cu_2Fe(CN)_6$



Curves 1-3 refer respectively to *N*/200-KCl, *N*/500- and *N*/1000 $BaCl_2$.

FIG. 14.

$Cu_2Fe(CN)_6$ *sol*.



1—*N*/60-KCl; 2—*N*/4000-$AlCl_3$; 3—*N*/5000-$AlCl_3$; 4—*N*/1000-$BaCl_2$; 5—*N*/50-KCl; 6—*N*/800-$BaCl_2$.

Selenium Sol.—(*i*) With KCl, curve 2, Fig. 10 is an exception to the concentration effect.

(*ii*) With $BaCl_2$ the concentration effect is pronounced (curve 1, Fig. 11). At lower concentrations there is at first a decrease followed by an increase in c. v. afterwards, when the time of observation is prolonged (curves 2, 3, 4, Fig. 11).

(*iii*) With aluminium chloride, the concentration effect is quite pronounced after about half an hour. On inspection of Figs. 9, 11 and 12, the valency effect is found to be quite pronounced.

Uranyl Ferrocyanide Sol.—The valency effect is absent (Fig. 15).

Copper Ferrocyanide Sol.—(*i*) With (*N*/50) KCl, variations in c. v. are irregular (*cf.* Fig. 14).

(*ii*) The concentration effect as well as the valency effect is marked with $BaCl_2$ and $AlCl_3$ in most cases. Potassium chloride again gives an exception.

(*iii*) The concentration effect is pronounced (curves 2 and 3, Fig. 13).

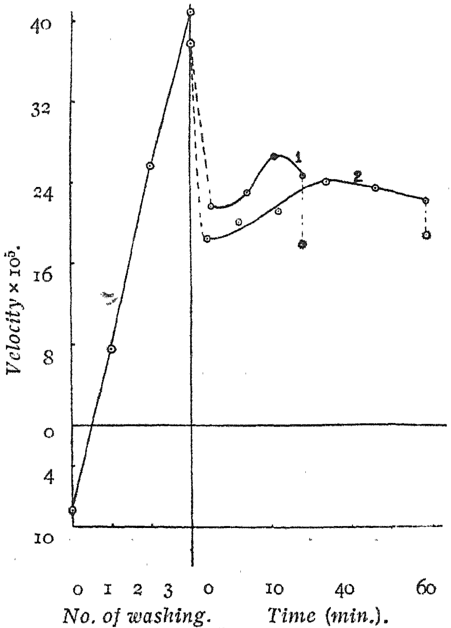
Ferric hydroxide Hydrosol.—(*i*) The concentration effect is observed with KCl (curves 1, 2, and 3, Fig. 16), but not with K-oxalate (curves 6, 7 and 8, Fig. 16).

The idea of the reproducibility of each curve may be formed from Fig. 17, where the C.V. values in the As_2S_3 sol and *N*/12-KCl have been repeated.

FIG. 15.

$(UO_2)_2\,Fe(CN)_6$.

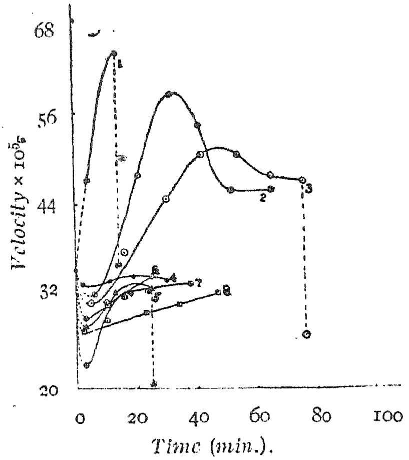
ppt. *sol.*
Peptisation Coagulation



1—*N*/500-$BaCl_2$; 2—*N*/300-KCl.

FIG. 16.

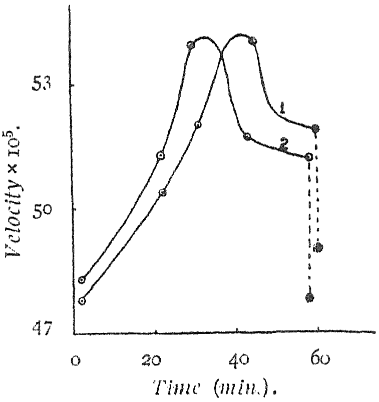
$Fe(OH)_3$ *sol.*



1—N/KCl; 2—N/2-KCl; 3—N/2-KCl; 4—N/800-K-citrate; 5—N-$BaCl_2$; 6-N/600 K-oxalate; 7—N/525-K-oxalate; 8—N/550-K-oxalate.

FIG. 17.

As_2S_3 *sol.*



N/12-KCl.

DISCUSSION.

It would appear from the curves that the rate of cataphoresis runs somewhat parallel to the rate of coagulation and that none of the theories of cataphoresis is sufficient to explain these results of diverse character, for the simple reason that in the theories of cataphoresis in presence of electrolytes, no account has so far been taken of the equilibrium between the process of aggregation and de-aggregation of the colloidal particles (*vide supra*).

The kinetics of the coagulation of a colloid by an electrolyte has been dealt with theoretically by Smoluchowski (*Kolloid Z.*, 1916, **18**, 190) and various attempts to verify it experimentally have been made by different investigators, notably by Westgren and Reitstöter (*Z. physikal. Chem.*, 1918, **92**, 750), Mukherjee and co-workers (*J. Chem. Soc.*, 1920, **117**, 1564; 1924, **125**, 785), Desai and co-workers (*Trans. Faraday Soc.*, 1928, **24**, 181; *Kolloid Chem. Beih.*, 1928, **26**, 357; *Trans. Faraday Soc.*, 1930, **26**, 138) and recently by Joshi and co-workers (*J. Indian Chem. Soc.*, 1931, **8**, 11, 337; 1932, **9**, 157; 1933, **10**, 329; *J. Indian Chem. Soc., Ray Comm. Vol.*, 1931, p. 41).

As a result of these investigations it has been found that (*i*) With low concentrations of electrolytes, initially Smoluchowski's equation holds good but afterwards there are marked deviations. These are not the only results contrary to the expectations from the theory of Smoluchowski, but great irregularities and discontinuities in the coagulation process have been reported (Joshi and co-workers, *loc. cit.*).

(*ii*) At high concentrations of electrolytes, Smoluchowski's equation has been generally found to hold good.

As has been pointed out under the section "Results" that very often at the high concentrations of electrolytes, the percentage increase in c. v. with time is larger as the concentration of the electrolyte increases and that higher the valency of the precipitating ions, the greater is the percentage increment. This is to be expected from the theory of Smoluchowski on the basis of *the hypothesis suggested by us (loc. cit.) that the increase in* c. v. *is the outcome of the aggregation of the particles.* The higher the stage of aggregation or perhaps the more closely and intensely the primary particles are held in the aggregate, the greater is the percentage increase in the c. v. It is of interest to note that a possible explanation of the failure of Smoluchowski's theory at concentrations other than those producing rapid coagulation consists in the inhibiting effect of an increase in the c. v., *i.e.*, potential of the double layer (*cf.* Mukherjee and Majumdar, *loc. cit.*). A correlation in the observed changes in c. v. with the kinetics of the coagulation is very much desirable and it is hoped to deal with this aspect in a future communication.

The rate of coagulation by an electrolyte or the coagulating power of an electrolyte is known to depend on the quality of the sol including its contents of free electrolytes, specially of ions which are constituents of the colloidal substance. Dhar and co-workers (*J. Indian Chem. Soc.*, 1929, **6**, 31) report that the purer the sol, the less is the valency effect. In case of uranium and copper ferrocyanide hydrosols which perhaps contain only small amounts of free electrolytes as would appear from their method of preparation and the specific conductivity of the order of 10^{-5} mho., the valency effect as observed by us in other cases disappears.

In the case of other sols the valency effect is quite marked though concentration effect is not so regularly pronounced. But the specific conductivities of other sols where the valency effect is quite marked are not materially different from that of the copper and uranium ferrocyanide sol, though it is somewhat larger. Further, with these sols the concentration effect is not so well pronounced. Potassium chloride quite often forms an exception to the concentration effect and hydrogen chloride shows a very great increase in the c. v. with time. The curves for arsenious sulphide (*cf.* Figs. 5 and 6) show greater irregularity than similar curves for other sols. This is presumably due to complex nature of As_2S_3 sol and to the presence of polythionic acids and colloidal sulphur (Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, **2**, 296).

It would thus appear that the cataphoretic velocity of a colloid depends more on the condition of aggregation of the colloids than on the nature and concentration of the electrolytes taken, these latter two affecting the c. v. of a colloid in so far as they do it by producing a certain stage of aggregation in the system. Thus it also follows as a corollary that the postulate of the coagulation of a colloid taking place at a critical potential even in presence of multivalent precipitating ions is quite untenable in view of the facts presented in this and other papers (*cf.* Mukherjee Chaudhury and Ghosh, *loc. cit.*).

SUMMARY.

The observations so far made may be summarised as follows:—

1. In presence of coagulating concentrations of electrolytes

(*a*) The higher the valency of the precipitating ion, the greater is the percentage increase in c. v. observed with time.

(*b*) The higher the concentration of the electrolyte taken, the greater is the percentage increase in c. v. observed with time.

(*c*) In some sols where the purity of the sol is comparatively greater, effect (*a*) disappears—just as the valency effect on the coagulating powers of electrolytes disappears in the case of extremely pure sols.

2. In the region of slow coagulation, *i.e.*, with low concentrations of electrolytes there are discontinuities of an irregular nature observed in the variation of c. v. with time, similar to those observed in the rate of coagulation of colloids with low concentrations of electrolytes.

3. Moreover, the variation of c. v. with time in presence of an electrolyte appears to depend on (*i*) the nature of the sol; (*ii*) the nature of the electrolyte added and (*iii*) the electrolytic content of the sol—conditions on which also depends the rate of coagulation of different colloids in presence of various electrolytes.

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Studies in the Coagulation of Colloids. Part XIV. Coagulation of Colloid Arsenious Sulphide by Mercuric Chloride. Inadmissibility of Viscosity and Transparency as General Criteria of Coagulation.

By Shridhar Sarvottam Joshi and Sadashiv S. Kulkarni.

Arising out of work which has been in progress for some time in these laboratories, on the coagulative powers of aqueous solutions of mercury chloride relative to those of other electrolytes to be published shortly, was the question of the variation of the viscosity and of the light transparency of a sol subjected to coagulation by mercury chloride. Reference to the literature showed that the rôle of this electrolyte as a coagulant has not received the adequate attention, which a consideration of some of its physico-chemical properties suggests. The present work was therefore undertaken with a view to supply the deficiency of our knowledge in this line.

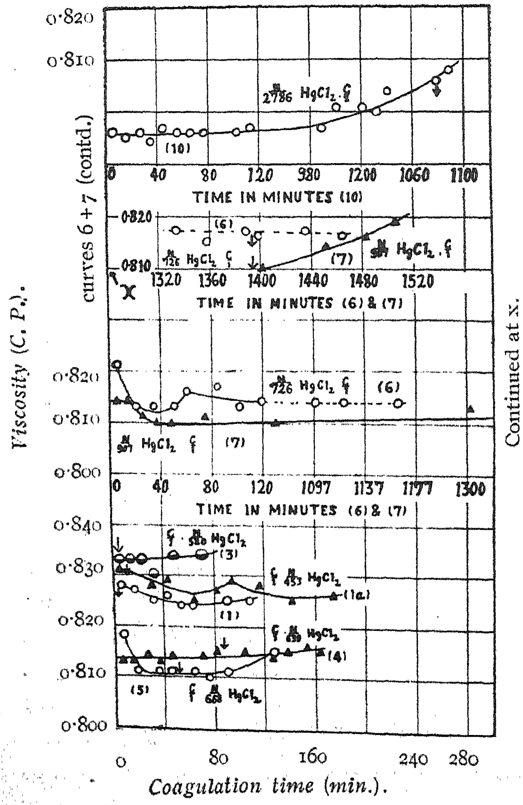
EXPERIMENTAL.

The sol was prepared by adding in small quantities from a paste of arsenious acid to twice distilled water which was kept boiling. After filtering and allowing it to cool, a current of hydrogen sulphide, washed previously by leading through water, was passed very slowly and with continuous shaking. The excess of the gas was then driven off by a current of hydrogen. The colloid content was estimated by a method described previously (Joshi and Nanjappa, *J. Indian Chem. Soc.*, 1934, **11**, 135). It was 18·1 g. of arsenious sulphide per litre. Equal volumes of the colloid and of the coagulator solution were allowed to attain the temperature of the thermostat, *viz.*, $30 \pm 0{\cdot}1°$, and mixed in the Scarpa tube of the viscometer. Three concentrations for the colloid *in the coagulation mixture* were employed in experiments referred to in Figs. 1-4, *viz.*, $C/1 = 9{\cdot}03$, $C/2 = 4{\cdot}51$ and $C/8 = 1{\cdot}13$ g. arsenious sulphide per litre. The viscosity was measured by the Scarpa's method with modifications as described previously (Joshi and Menon, *ibid.*, 1933, **10**, 599). The suction applied to the liquid to be examined was kept constant at 31·5±0·01 cm. of water in all the experiments. This pressure was such as gave approximately equal times for the rise and the fall of the liquid through the capillary in the Scarpa tube, as required by the theory of the instrument for maximum accuracy *(loc. cit.)*. It is known that particularly in the case of colloids, validity of the data for viscosity depends upon whether the measurements were made under conditions of *viscous flow*. This was ascertained in the present work by the observation that the time for rise for the colloid used under a large number of pressures in the neighbourhood of the above value was clearly a *linear* function of the applied pressure. The constant k involved in the equation,

$$\eta = k.\frac{t_1 t_2}{t_1 + t_2},$$

(where t_1, t_2 and η are the the times for the rise, the fall of the liquid and its viscosity respectively) was found to be 0·007033, when η for water was taken to be 0·7958 C.P. (*cf.* Bingham, "Fluidity and Plasticity," 1922, p. 339). These measurements were continued till the appearance of the coagulum as discrete particles on the walls of the viscometer became just perceptible. In the majority of cases this stage was observable easily and fairly unambiguously, and has been indicated by an arrow on the viscosity-time curve, when the viscosity measurements were continued beyond this stage. The degree of reproducibility of these results using pure liquids was easily 1-2 in 1000.

FIG. 1.



Variations less than at least ten times this quantity have not been considered in the data recorded in this paper. The results for the change of viscosity, when the colloid concentration was varied up to eightfold and that of mercury chloride varied in the range $N/500$ to $N/2000$, are shown graphically in Figs. 1 and 2. It might be added that use of concentrations higher than $N/500$ produced coagulations which were too quick for viscosity and other measurements. Viscosity measurements were also made during coagulations due to mercury chloride mixed with *small* amounts of other electrolytes; of these only one typical result, when $N/150$-KCl was added, is shown graphically by curve 17 in Fig. 2. Curves shown in Fig. 3 show just a few typical cases of a much greater number of curves obtained showing the change of viscosity when the coagulants were solutions of potassium and cadmium chloride under the same conditions, for comparison with coagulations by mercuric chloride.

In view of the unexpected results obtained in respect of viscosity, it was thought desirable to examine the variation of another property, transparency which has been so widely employed in measurements of coagulation. This has been determined by two different methods. The first series of experiments, some of which are represented by the time-transparency curves in Fig. 4, were carried out using a thermopile, whose readings on light let through in the coagulating sol were taken by means of a sensitive Broca galvanometer. Complete details as regards the method of observation, the precautions taken are reported in an earlier paper (Part XIII) in this series. In the next series of experiments, the opacity of the coagulating sol was determined directly by means of a Duboscq colorimeter. The apparatus consisted essentially of two similar tubes illuminated from the bottom. Each of these carried a fairly well fitting empty tube moving co-axially. The underfaces of the inside tubes showed the same position on the vertical scale fixed on the instrument, when the outer tubes were symmetrically illuminated by a given beam of light and when the same liquid was present in both the outer tubes, the emergent light from both the tubes being matched for equality of intensity through an eye-piece. In actual measurements, one of the tubes was filled with a convenient volume of the colloid diluted with an equal volume of pure water. The other limb contained the same amount of the colloid mixed with an equal volume of any of the coagulating solutions. By shifting the tube in the latter therefore, a measure of the opacity of the coagulating sol was obtained relative to that of the colloid diluted with water in the difference in the positions of the two columns, when matching. These results with mercuric and potassium chlorides are shown by curves in Fig. 5.

DISCUSSION.

It has been almost a tacit assumption with colloid chemists that coagulation produces necessarily an increase of viscosity (and of opacity, *vide infra*), and many workers have supposed that the last quantity is a measure of the corresponding degree of coagulation. The viscosity-time curves in Figs. 1 and 2 show that coagulations with mercuric chloride negative this generalisation, in failing to show an over-all rise of viscosity, in by far the majority of cases. Two features are, however, noticeable in almost all the curves :

(*i*) There is an initial fall of viscosity which has been observed previously in numerous coagulations with different sols and coagulants (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 323; Joshi and Menon, *ibid.*, p. 599; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133; Joshi and Iyengar, *ibid.*, pp. 555, 574; Joshi and Panikkar, *ibid.*, p. 797; *cf.* also, *Proc. Acad. Sci., U. P.*, 1935, **5**, 41; *J. chim. phys.*, 1935, **32**, 455).

(*ii*) The progress of the viscosity change during coagulation is '*zonal*,' that is, occurs through breaks, although a given coagulation-time curve does not show a sensible net rise of viscosity except in curves 7 and 10 in Fig. 1, where the rise sets in only after an extremely long time after the start of coagulation, *viz.*, 980 and 1400 minutes respectively.

It is interesting to compare the curves in Figs. 1 and 2 for mercury chloride with those in Fig. 3 due to cadmium and potassium chlorides. The difference is well marked. With higher concentrations of these electrolytes, the viscosity increases on the whole during coagulation, the increase being '*zonal*' or discontinuous. With low concentrations there is no net increase of viscosity, but merely a number of breaks, which is precisely in agreement with earlier results (Joshi and co-workers, *loc. cit.*). *The abnormality in the case of mercury chloride is revealed by the fact, that even if a higher concentration of this coagulator is used, what is produced is flocculation which comes down as a precipitate in due time, but no rise of viscosity, so familiar in coagulation phenomena.* It is also interesting to consider the curve No. 17

FIG. 2.

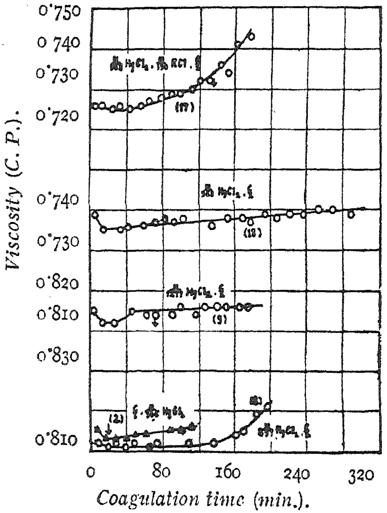


FIG. 3.

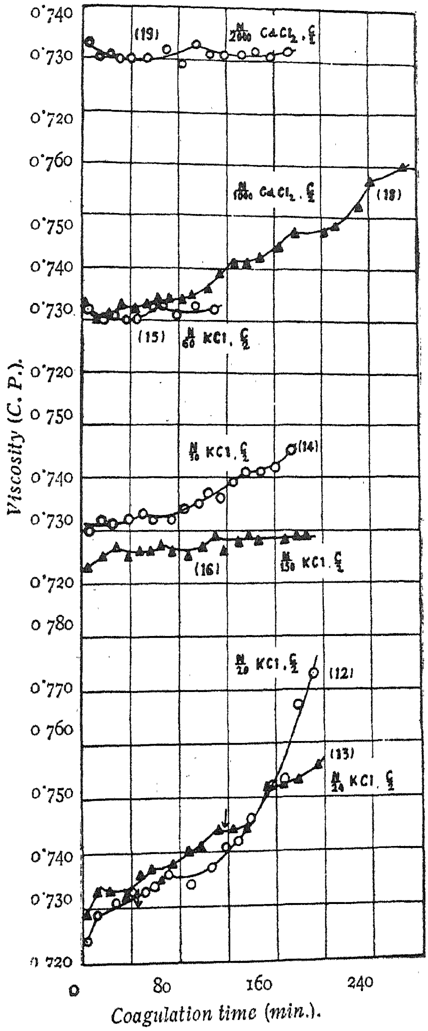
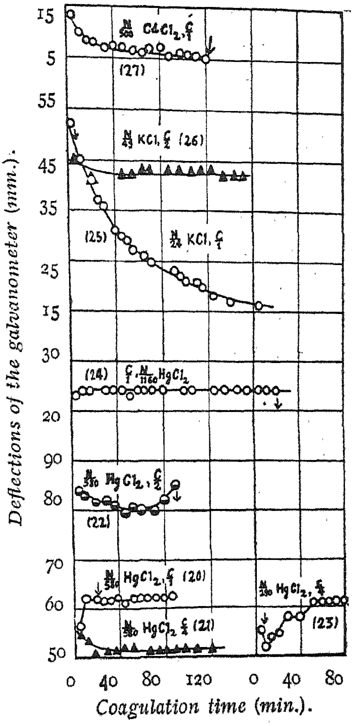
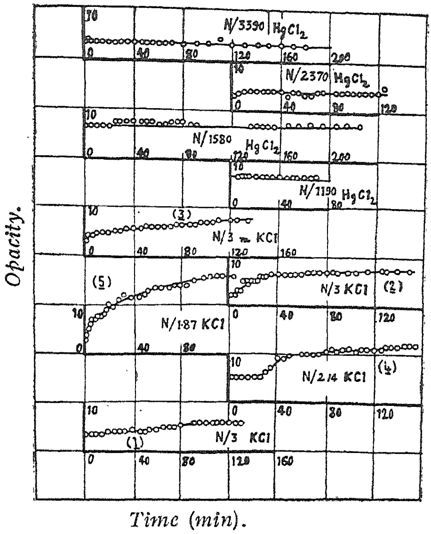


FIG. 4.



in Fig. 2. When mixed with $N/962$-$HgCl_2$ only, it was observed that a curve only with an initial fall and a number of breaks, but without an over-all increase of viscosity could be observed even after very considerable time. Essentially the same result was obtained when $N/150$-KCl was used as a coagulant (*cf.* curve 16, Fig. 3). When, however, the two electrolytes were mixed, the curve is wholly normal; it shows an appreciable over-all rise in viscosity during a comparatively shorter period; the flocculation also was observed comparatively early. It might be mentioned that detailed studies were made of the viscosity changes in two other colloids, *viz.*, colloid manganese dioxide and colloid antimony sulphide in the presence of mercuric chloride to see if these also showed an absence of viscosity rise. The results showed that these sols behaved normally, that is, they always showed a net rise in viscosity when the coagulant was reasonably concentrated. The conclusion is, therefore, suggested that the above results seem to be a peculiarity of the arsenious sulphide sol with mercury chloride as the coagulant. It might be also mentioned at this stage that the coagulum obtained in experiments with mercuric chloride, was examined outside the viscometer; it felt to be comparatively more *gritty*, and unlike the soft, almost filamented and gelatin-like mass observed usually. It is suggested as a tentative hypothesis that this absence of viscosity rise might be due appreciably to the above character of coagulum, and experiments are now in progress to obtain more information in regard to this possibility. Results have been obtained previously (Joshi and Nanjappa, Joshi and Iyengar, *loc. cit.*) to show that in a number of coagulations, the viscosity showed antinormal variation, *viz.*, a very marked and over-all diminution, the curve being *zonal*. These results together with the present findings suggest that it is not unlikely that the rise of viscosity might not depend entirely on such a single micellar property as the charge, the size, etc., but rather on some additional factors leading to a kind of meshwork-like or aggregate structure, which grows in the coagulating system from the very incipience of the change.

FIG. 5.



Curves 1-5 refer respectively to 0·67 g, 1·13 g., 2·25 g., 0·57 g. and 0·57 g. As_2S_3 per litre. Curves with $HgCl_2$ refer to 2·25 g. per litre.

It is interesting to see (from the curves in Figs. 4 and 5) that the variations of transparency (Fig. 4) and of opacity (Fig. 5) during coagulations with mercuric chloride show a striking parallelism with the corresponding results of viscosity measurements, *viz.*, that both these quantities do not change. It must be emphasised that the measurements of these related quantities, *viz.*, transparency and opacity were made by completely independent methods. Their mutual agreement is, therefore, of importance. The rise in transparency shown by curves 20 and 23 in Fig. 4 was due to the fact that the precipitation of the coagulum, set in almost from the start of coagulation as shown by the arrow on the curve, with the result that the transparency of the system approached that of the continuous medium, *viz.*, water. As in the viscosity results, this finding is peculiar to the use of the above coagulant; this is shown by a few typical curves (No. 25, 26 and 27 in Fig. 4 and No. 5 in Fig. 5), when other coagulants like cadmium and potassium chlorides were employed, under the same conditions. Also as observed in the case of viscosity measurements, transparency (Fig. 4) and the inverse of opacity (Fig. 5) do not appreciably diminish if only a low concentration of the normal coagulant say potassium chloride is employed (*vide* curve 26, Fig. 4, curve 1, Fig. 5). As soon as, however, its concentration is raised, we get the familiar reduction of transparency (*cf.* curve 25, Fig. 4) and rise of opacity (curves 4, 5 in Fig. 5). The abnormality of mercury chloride is once more brought out by the fact that the transparency does not diminish (and the opacity does not rise) even though the concentration of this coagulant is increased. Under the latter condition it produces flocculation and the precipitate actually tends to settle down, that is, mercury chloride is effective in producing coagulation but not in giving rise to the familiar optical effect, usually regarded as characteristic of coagulation. Further work in this line has shown that the above results in viscosity and transparency measurements are but two of the evidences—which are being accumulated in these laboratories—of the anomalies in the behaviour of mercury salts when used as coagulants. These results will be published shortly. From analogy with the results of viscosity mentioned above, it is suggested that transparency also at any rate in the case of colloids, might be more a macroscopic and body property, than a singular function of such micellar constants like charge, size and so forth, variable during coagulation.

The view has been emphasised in earlier papers (*loc. cit.*) that contrary to the simple mechanism postulated in Smoluchowski's theory, coagulation might consist of a series of micellar and allied changes, and that a given property selected for measuring coagulation might not be sensitive to some of these changes. The present results of the non-variation of viscosity, transparency and opacity, measured separately during coagulations with mercury chloride, give experimental support to the above view. Further work is now needed to elucidate in general the principal determinants of the above quantities, *viz.*, viscosity, transparency (and opacity) in coagulating sols. If, however, during a given stage of coagulation, the constituent changes taking place are such as not to influence the property selected for measuring coagulation, then the corresponding section of the coagulation-time curve will have a reduced gradient characteristic of the so-called **S**-shape, and give but spurious evidence of *autocatalysis* (*cf.* curve 4, Fig. 5). This possibility is of some considerable significance since not a few workers have tried to show that *autocatalysis* might be a *general* description of the coagulation phenomena.

SUMMARY.

1. Measurements have been made of the viscosity, transparency and of the opacity of colloid arsenious sulphide sols of varying colloid contents in the presence of mercury chloride. It has been found that the above quantities do not show an over-all change as a result of coagulation, with the above coagulant.

2. Normal variations in the above properties were observed when cadmium and potassium chlorides were used under the same conditions, and also when but small quantities of them were added to mercury chloride used as a coagulant.

3. Further evidence is obtained to support the view suggested earlier that coagulation is not time-continuous but *'zonal,'* and that this feature becomes more pronounced the *slower* the change.

4. It is suggested that both the viscosity and transparency (and therefore opacity) in colloids are functions partly of micellar constants such as the charge, size and specially the shape, etc., and of certain bulk or macroscopic properties of the system as a whole and that the latter might be the more potent factor.

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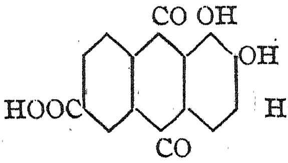
Studies in the Anthraquinone Series. Attempts to synthesise Anthraquinone Carboxylic Acids of the Morindone Type.

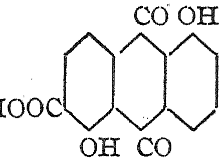
BY P. C. MITTER AND (MISS) TANIMA SEN-GUPTA.

Among the naturally occurring anthraquinone derivatives, carboxylic acids are known only in the madder and emodin groups. The acids occurring in madder are munjisthin and pseudo-purpurin while those belonging to the emodin group are rhein and emodic acid. It appeared to us to be of interest to synthesise acids of the morindone type, which might occur in natural products.

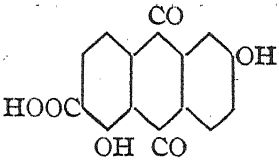
An anthraquinone derivative of the morindone type containing a carboxyl group and not less than two hydroxyl groups may have one or other of four alternative formulæ A to D.



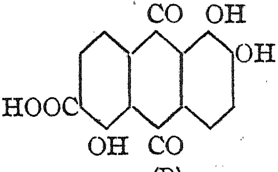
(A)



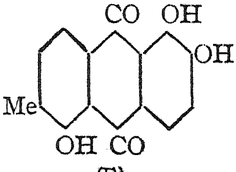
(B)



(C)



(D)

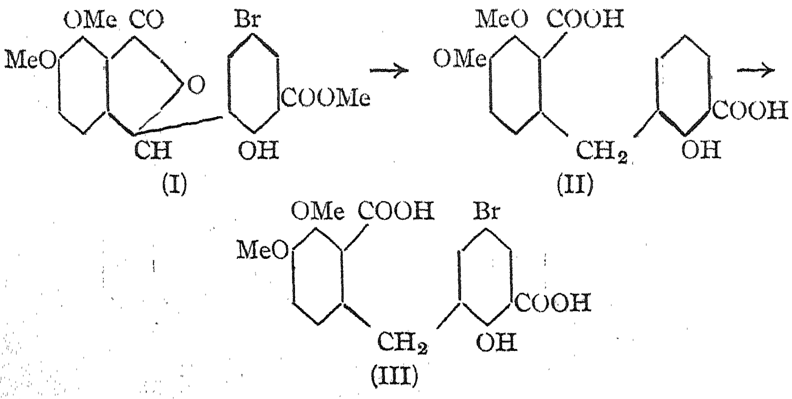


(E)
Morindone

We have synthesised the β-methyl ether of (A) by oxidising 1-acetoxy-2-methoxy-6-methylanthraquinone (Mitter and Biswas, *J. Indian Chem. Soc.*, 1928, **5**, 776) with chromic acid and deacetylating the product. It forms red silky needles, melting at 195°.

Our next idea was to synthesise the acid (D). Now the usual laboratory oxidation processes are not suitable for the oxidation of methyl groups, with adjacent hydroxyl groups, into carboxyl groups (Mitter and Sen, *J. Indian Chem. Soc.*, 1928, **5**, 635). In this connection, mention may also be made of the case of munjisthin, which could not be obtained by the direct oxidation of rubiadin. We, therefore, tried a procedure similar to that adopted by Jacobson and Adams for the synthesis of a derivative of morindone (*J. Amer. Chem. Soc.*, 1924, **46**, 2788).

Opianic acid was condensed with methyl 5-bromosalicylate in presence of sulphuric acid, when 5:6-dimethoxy-2 (2′-hydroxy-3′-carboxy-5′-bromophenyl) phthalide (I) was obtained as white crystals, m.p. 215°. This was reduced with zinc dust and caustic soda in boiling solution under mechanical stirring for 15 hours. The dibasic acid so obtained (II) melted at 225°. Several ring-closure experiments were tried with (II) with a view to obtain the corresponding anthrone. It was treated with sulphuric acid in the cold as well as with heating. In the former case it remained unchanged while in the latter complete sulphonation took place. We also tried phosphorus pentoxide but without success. It is well known that hydroxy compounds having *para*-positions to the hydroxyl groups free, are easily sulphonated. So the acid was brominated, when a monobromo derivative, presumably the *p*-bromo derivative (*cf.* Jacobson and Adams, *loc. cit.*) melting at 210°, was obtained. Ring-closure experiments with this compound also met with no better success.



(I)

(II)

(III)

EXPERIMENTAL.

5:6 - *Dimethoxy*-2-(2′ - *hydroxy* - 3′ - *carbomethoxy*-5′-*bromophenyl*)-*phthalide* (I).—Methyl 5-bromosalicylate (5 g.), opianic acid (3·6 g.) and sulphuric acid (13 c.c., 1 part of water in 6 parts of concentrated acid) were mixed thoroughly in a mortar and allowed to stand for 2 days when the mass became green. On adding water, heavy granular precipitate separated which, after washing with water, was crystallised from glacial acetic acid, m.p. 215°, yield 3 g. (Found: Br, 17·9. $C_{18}H_{15}O_7Br$ requires Br, 18·9 per cent).

An *acetyl* derivative was obtained on acetylation with acetic anhydride and pyridine, m.p. 210° after crystallisation from glacial acetic acid. (Found: Br, 17·26. $C_{20}H_{17}O_8Br$ requires Br, 17·20 per cent).

5:6-*Dimethoxy*- 2 - (2′-*hydroxy*-3′ - *carboxy*-5′ - *bromophenyl*) *phthalide*.—The phthalide (1 part) was refluxed with 10% KOH (5 parts) for 3 hours. On dilution and precipitation with hydrochloric acid, the acid was precipitated. It was crystallised from acetic acid, m.p. 253°. (Found: Br, 20·4. $C_{17}H_{13}O_7Br$ requires Br, 19·56 per cent).

5:6-*Dimethoxy*-2(2′-*hydroxy*-3′-*carboxybenzyl*)-*benzoic Acid* (II).—The phthalide (I) (5 g.), 10% NaOH solution (104 c.c.) and zinc (17 g.) were introduced into a three-necked flask fitted with a reflux condenser and a mechanical stirrer and the contents heated on a sand-bath under stirring for 15 hours. The excess of zinc was filtered off and concentrated hydrochloric acid added to the filtrate when a flocculent precipitate was formed. This was filtered, washed and dissolved in 10% soda solution. The filtrate was acidified, the precipitate washed free from hydrochloric acid and crystallised from dilute acetic acid, m.p. 225°, yield 2 g. (Found: C, 61·7; H, 5·06. $C_{17}H_{16}O_7$ requires C, 61·4; H, 4·85 per cent).

5 : 6- *Dimethoxy*-2(2′ - *hydroxy*-3′- *carboxy*-5′ - *bromobenzyl*) *benzoic Acid* (III).—The benzoylbenzoic acid (II) was dissolved in glacial acetic acid (50 c.c.) by heating and after cooling bromine (0·16 c.c.) was added. The mixture was left overnight and then diluted. The precipitate was filtered, washed and recrystallised from glacial acetic acid, m.p. 210°. (Found: Br, 19·6. $C_{17}H_{15}O_7Br$ requires Br, 19·4 per cent).

We offer our thanks to the Opium Agent, Government of India, for the free gift of narcotine which formed the starting material for the preparation of opianic acid.

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The Enzymes in Snake-venom. Part I. Their Action on Hæmoglobin and on Protein Solutions of Different p_H.

By B. N. Ghosh.

It has been recorded by several early investigators that venoms of many poisonous snakes can exert marked digestive action (in *vivo*) on animal tissues. Later on, this effect was found to be produced by some proteolytic enzymes present in the venom. Flexner and Noguchi (*Univ. Pennsylv. Med. Bull.*, 1902, **15**, 345), Delezenne (*Compt. rend.*, 1902, **135**, 329), Noc (*Ann. Inst. Pasteur*, 1904, **18**, 387), Launoy (*Compt. rend.*, 1902, **135**, 401), and Housey and Negrete (*Rev. Del. Inst. Bact. Buenos-Aires*, 1918, **1**, 341) observed that snake venom can hydrolyse proteins like gelatin, albumin, casein etc. Using casein and serum albumin as substrates, Launoy (*loc. cit.*) observed that with the venoms of cobra and of the vipera, the proteolysis stops when albumose is formed. It does not proceed so far as to form peptone. Recently Dunn (*J. Pharm. Exp. Therap.*, 1934, **50**, 386) noticed that venom of *Crotalus adamantus* can digest casein suspended in 0·2 N-sodium acetate more rapidly than casein of coagulated milk without the sodium acetate. It may be pointed out that the influence of the reaction of the medium on the activity of the enzymes (in snake-venom) has not been studied by any of the authors already mentioned. It is now recognised that proteases of animal origin can be separated into three groups, based on their activity in media of different p_H :

(*i*) The proteases which are active in distinctly acid range are analogous to pepsin.

(*ii*) Those which are active in the slightly alkaline range with an optimum at about p_H 8, are similar to trypsin.

(*iii*) Those which show optimum activity in the neighbourhood of p_H 5 are analogous to kathepsin.

It will be interesting to know to which of these groups the proteases in snake-venom belong. In the present paper the results obtained by studying the action of venoms of cobra (*Naja Naja*) and of Russell's viper on hæmoglobin and of cobra-venom on different proteins in media of different p_H values have been recorded.

EXPERIMENTAL.

Action of Cobra-venom on Proteins.

Stock solution of gelatin (5%), Merck's dried egg-albumin and casein were prepared in physiological saline (0·85% NaCl). The solutions were prepared the day before they were required for use and kept in a refrigerator at 4° with the addition of a few drops of toluene. The gelatin used was previously purified by electrodialysis. The casein solution was prepared by dissolving it in NaOH and then nearly neutralising the solution with dilute HCl.

A solution of cobra-venom (1%) in physiological saline was prepared a few hours before it was required for use. Its toxicity was tested by intramuscular injection into pigeons. It was found that 0·4 mg. of venom (dry weight) just kills a pigeon weighing between 300 to 320 g.

The extent of hydrolysis was followed by Willistätter's method of titration in 90% alcoholic solution with alcoholic caustic potash, using thymolphthalein as an indicator.

The p_H of the reaction media was maintained nearly constant by adding buffer solutions. Between p_H 2 to 5, citrate buffers were used and between p_H 6 to 9·6 phosphate and borate buffers were used. The stock protein solution (20 c.c.) were taken in an Erlenmeyer's flask and its p_H adjusted to the requisite volume by adding a few drops of NaOH or HCl solution according to need. To this solution, 10 c.c. of buffer solution of the same p_H were added. 10 C.c. of this buffered protein solution were placed in each of the two conical flasks. To one of the flasks, 2 c.c. of the solution and 8 c.c. of physiological saline were added. To the other flask which served as a control, 8 c.c. of physiological saline and 2 c.c. of the cobra-venom solution were added; the latter was previously heated for 50 minutes at 75°, to destroy the proteases present in it. To each of the flasks a few drops of toluene were added to prevent bacterial growth and they were placed in a thermostat at 35°. After suitable intervals of time, 5 c.c. portions of the solution were withdrawn and added to 45 c.c. of absolute alcohol to which 0·5 c.c. of 0·5% thymolphthalein solution in alcohol were previously added. The mixture was then immediately titrated with alcoholic potash. In another set of control experiments 10 c.c. of the buffered protein solution were mixed with 10 c.c. of 0·85% NaCl and incubated at 35°. After suitable intervals of time, 5 c.c. portions of this solution were titrated in the manner described above; but just before titration 0·5 c.c. of 1% cobra-venom solution was added to it. The two sets of control experiments were in satisfactory agreement with each other. The results obtained are recorded below. As the proteolytic power of the venom was found to be weak, the interval of time allowed for digestion was 24 hours. The action of trypsin on casein media of different p_H values was also studied for the purpose of comparison and the data are recorded in Table IV.

TABLE I.

Substrate used—gelatin.

p_H.	*N*/25-alcoholic KOH required to titrate		Diff. between columns 2 & 3.
	Active venom and substrate.	Control.	
2·0	6·60 c.c.	6·60 c.c.	0
4·0	4·20	4·25	−0·05
5·0	3·85	3·80	+0·05
5·5	3·65	3·50	+0·15
6·0	3·30	3·00	+0·30
7·0	3·10	2·60	+0·50
7·4	2·95	2·40	+0·55
7·8	2·80	2·20	+0·60
8·4	2·45	1·90	+0·55
9·0	2·10	1·70	+0·40

TABLE II.

Substrate used—egg-albumin.

p_H.	*N*/25-alcoholic KOH required to titrate		Diff. between columns 2 & 3.
	Active venom and substrate.	Control.	
6·0	3·30 c.c.	3·00 c.c.	0·30
7·0	2·98	2·50	0·48
8·0	2·65	2·10	0·55
9·2	2·00	1·60	0·40

TABLE III.

Substrate used—casein. Temp. of bath, 37°.

p_H.	N/25-alcoholic KOH required to titrate Active venom and substrate.	Control.	Diff. between columns 2 & 3.
6.0	3·55 c.c.	3·00 c.c.	0·55
6·4	3·52	2·85	0·67
7·0	3·20	2·50	0·70
8·2	2·80	2·15	0·65
9·0	2·25	1·65	0·60

TABLE IV.

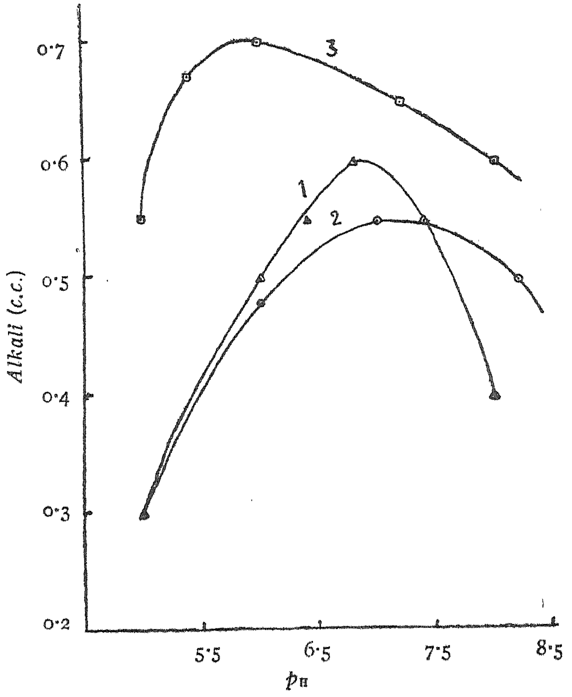
Substrate—casein. Enzyme—trypsin.

20 C.c. of the reaction mixture contained 2 c.c. of 0·25% trypsin soln.

p_H.	N/25-alcoholic KOH required to titrate Trypsin and casein.	Control.	Diff. between columns 2 & 3.
5·5	4·15 c.c.	3·50 c.c.	0·65
6·6	4·25	2·90	1·35
7·6	3·60	2·45	1·15
8·6	2·80	1·80	1·00

It will be noticed from Fig. 1. and also from the data given in the tables that with gelatin and egg-albumin as substrate, the proteolytic enzyme in cobra-venom has its optimum activity at p_H 8 or near about it, while with the casein as substrate, the optimum activity of the enzyme isin the neighbourhood of p_H 6·6. The results are in agreement with the action of trypsin on these substrates as observed by Long and Hull (*J. Amer. Chem. Soc.*, 1917, **39**, 1051). There is, however, some doubt as to the p_H of casein suspension at which trypsin possesses its optimum activity. According to Cole ("Practical Physiological Chemistry," 1928, p. 226) with casein also, the optimum activity of trypsin is in the neighbourhood of p_H 8·0 and not 6·6. The action of trypsin on casein suspension was, therefore, studied by the author and the results obtained are recorded in Table IV. The data show that the optimum activity is near about p_H 6·6. It may, therefore, be concluded that as far as the dependence of activity on the reaction of the substrate solution is concerned, the behaviour of the protease in cobra-venom is similar to that of trypsin. Further work in this line with venoms of cobra and of other snakes are in progress.

FIG. 1.



Curves 1-3 refer respectively to gelatin, egg-albumin and casein.

Action of Venoms of Cobra and of Russell's Viper on Hæmoglobin.

In the postmortem examination of the victims of snake-bite, it has been observed by several workers that the blood appeared somewhat dark. To obtain further information on this point, the action of snake-venom on hæmoglobin was studied. A thick suspension (0·4 c.c.) of red blood corpuscles of horse was added to 4 c.c. of sterilised distilled water, whereby the corpuscles were hæmolysed. Hæmoglobin solution (1 c.c.) was poured to each of the three test tubes. To one of these tubes, 1 c.c. of an 1 % cobra-venom solution and to another 1 c.c. of an 1% Russell's viper-venom were added. To the third tube, which served as control, one c.c. of 0·85 % NaCl was added. After 16 hours, the contents of the tubes were suitably diluted and examined spectroscopically. Distinct absorption band of methæmoglobin at 630 $\mu\mu$ in the red was noticed in the two tubes treated respectively with venoms of cobra and of Russel's viper. The control did not show any such band. It is thus evident that these venoms contain either an oxidising agent similar to $K_3Fe(CN)_6$ or an enzyme which can cause the oxidation of hæmoglobin to methæmoglobin.

SUMMARY.

1. With gelatin and egg-albumin as substrates the protease in cobra-venom was found to possess its optimum activity between p_H 7·8 to 8·0.

2. With casein as substrate the optimum activity of trypsin as also of the protease in cobra-venom was found to be in the neighbourhood of p_H 6·6.

3. The venoms of cobra and of Russell's viper can bring about the oxidation of hæmoglobin to methæmoglobin.

In conclusion I wish to express my grateful thanks to Sir P. C. Ray for the laboratory facilities offered. I also thank the Director of the Haffkine Institute, Bombay for supplying the venoms at a reduced price.

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On the Study of Polyhalides. Part IV. Formation and Dissociation of Polyhalides of Ammonium and Substituted Ammonium Bases.

BY SUSIL KUMAR RAY AND RAMA RANJAN BHATTACHARYA.

Although some of the stable polyhalides of ammonium and substituted ammonium bases were known for a long time, no systematic work on equilibrium or solubility relation appears to have been made (*cf.* Johnson, *J. Chem. Soc.*, 1878, **33**, 397). Tinkler (*ibid.*, 1908, **93**, 1611), Rae (*J. Amer. Chem. Soc.*, 1913, **45**, 1725), Chattaway and Hoyle (*J. Chem. Soc.*, 1923, **123**, 654) prepared and studied the properties of the compounds of the type $N\cdot(Alk)_4\cdot Hal_n$ (where n is 3, 5, 7 or 9) but neither the degree of dissociation nor the heat of formation was studied. Reade and collaborators (*ibid.*, 1923, **123**, 143; 1924, **125**, 157; 1926, 2529) studied the preparation of a large number of quarternary ammonium polyhalides; Gray and Dakers (*Phil. Mag.*, 1931, **11**, 81) prepared and measured the diamagnetism of polyhalides of Me_4N, Et_4N, etc. With a view to obtaining quantitative information regarding the various polyhalides of ammonium and substituted ammonium bases, the present investigation was undertaken.

In the present paper, the formation and dissociation of chlorodibromide, chlorodi-iodide, fluorodi-iodide, bromodi-iodide, tri-iodide and polybromide of ammonium, bromodi-iodide of ethylpyridinium, tri-iodide of tetramethylammonium and tribromide of tetramethylammonium were studied by means of the solubility method. The solubility of bromine in ethylpyridinium bromide and that of iodine in tetraethyl bromide and iodide and in ethylpyridinium iodide have also been determined but the formation of the complex polyhalide can not be deduced from the results.

The method adopted for the determination of the solubility was similar to that described in the previous part of this series (Ray, *J. Indian Chem. Soc.*, 1934, **11**, 115). Any change in the solubility of halogens in presence of different cations or in the degree of dissociation of the halides in presence of dissolved halogens was neglected. It is further assumed that any complex polyhalide that might be formed is dissociated electrolytically almost to the same extent as the simple halide and behaves in all respect like the simple halide ion.

From the increased solubility of the halogens in the solutions of the different halides studied, it may be concluded that the increased solubility is due to the combination of a part of dissolved halogen with the halogen ion of the halide forming the polyhalide. Attempts to apply the law of mass action to systems like these can not be expected to succeed and there is no reason to suppose that the formation of any particular polyhalide represents the sole action at any particular concentration. However, over a certain range of concentration, the value of the equilibrium constant, calculated on the assumption that trihalides are formed, are found to be fairly constant. In the case of the reactions between bromine and bromides, the equilibrium constant calculated on the assumption of the formation of the tribromide is found to vary widely but better results are obtained by calculating on the assumption of the formation of the pentabromide, though the results are by no means constant. In the case of pyridine-ethyl bromide and tetraethylammonium bromide, the equilibrium constants calculated on the assumption of the formation of tribromides or pentabromides do not give a constant value owing probably to the fact that various other polybromides are formed to a more or less extent. This agrees with the fact that the tendency to the formation of higher polyhalides is greater in the case of complexes where all the halogen atoms are of the same kind (Ray, *loc. cit.*).

Owing to the reaction between bromine and fluoride, the solubility could not be determined. The reaction between iodine and fluoride was studied by the solubility method and an approximately steady value for the equilibrium constants were obtained although Carter and Hoskins (*J. Chem. Soc.*, 1929, 580) could not determine the solubility owing to the reaction between iodine and fluoride. Tinkler (*loc. cit.*) also found no change in the ultraviolet absorption spectra of iodine by the addition of (Na, K or) NH_4F and concluded that probably no combination took place between iodine and fluoride. The present investigation, though does not give any constant value for the equilibrium constant, indicates that probably some combination takes place between iodine and fluoride. In the case of tetraethylammonium bromide and iodine and pyridine-ethyl iodide, a red precipitate was formed on the addition of iodine and the solubility of iodine was depressed. From this it appears that the compound precipitated contains most of the iodine that had dissolved in the water and is probably the required halide. Bromodi-iodide of pyridine-ethyl gave a black, viscous and oily liquid on the addition of iodine though in these cases the solubility was not depressed. In the case of tribromides of pyridine-ethyl and tetraethylammonium bases, the peculiar fact was noticed that on the addition of bromine a yellow precipitate gradually dissolved and in this case also the solubility was not depressed. Here as has already been pointed out the values of the equilibrium constant was by no means constant. Definite conclusions regarding the peculiarities noticed could not be drawn without further work.

The results of the investigations are given in the following tables. The degree of dissociation of the halides were calculated, unless otherwise mentioned, from the equivalent conductivities as given in the International Critical Table of Physical Constants.

TABLE I.

Formation of NH_4ClBr_2. Temp., 25°.

Halide conc.	Degree of dissociation.	Solubility of Br_2 in sat. soln.	Equilib. const. K.
4·0*N*	0·65	1·98 g/10 c.c.	3·47
2·0	0·70	1·26	3·80
1·0	0·74	0·87	4·71
0·5	0·77	0·60	4·70
0·25	0·80	0·46	4·70
0·125	0·84	0·39	4·74
0	—	0·30	—
			Mean 4·716*

TABLE II.

Formation of NH_4ClI_2. Temp., 25°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln.	Equilib. const. K
4·0*N*	0·65	0·02 g./10 c.c.	2·58
2·0	0·70	0·01	2·57
1·0	0·74	0·01	2·56
0·5	0·77	0·007	2·58
0·25	0·80	0·006	2·76
0·125	0·84	0·005	2·76
—	—	0·03	—
			Mean 2·576

* In calculating mean values, only those values which are nearly constant were considered.

TABLE III.

Formation of NH_4BrI_2. Temp., 30°.

Halide conc.	Degree of disso-ciation.	Solubility of I_2 in sat. soln.	Equilib. const. K.
4·0 N	0·68	0·33 g./10 c.c.	32·99
2·0	0·73	0·10	17·33
1·0	0·76	0·05	16·79
0·5	0·79	0·02	16·58
0·25	0·81	0·01	16·68
0·125	0·84	0·01	16·61
0·0625	0·88	0·007	16·69
0	—	0·003877	—
			Mean 16·67

TABLE IV.

Formation of ammonium polybromide. Temp., 30°.

Halide conc.	Degree of disso-ciation.	Solubility of Br_2 in sat. sol.	Equilib. const. K (Calc. as Br_5).
4·0 N	0·68	3·37 g./10 c.c.	12·33
2·0	0·73	1·28	9·34
1·0	0·76	1·21	8·46
0·5	0·79	0·91	8·20
0·25	0·81	0·76	8·00
0·125	0·84	0·69	7·98
0·0625	0·88	0·65	7·41
0	—	0·30	—
			Mean 8·165

TABLE V.

Formation of NH_4I_3. Temp., 30°.

Halide conc.	Degree of disso-ciation.	Solubility of I_2 in sat. soln.	Equilib. const. K.
4·0 N	0·69	2·89 g./10 c.c.	454·6
2·0	0·76	1·62	443·0
1·0	0·78	0·79	428·3
0·5	0·80	0·40	426·2
0·25	0·82	0·21	425·7
0·125	0·85	0·11	427·6
0·0625	0·88	0·05	427·8
0·03125	0·91	0·03	426·9
0	—	0·003	—
			Mean 427·1

TABLE VI.

Formation of NH_4Et_2. Temp., 25°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln.	Equilib. const. *K*.
4·0 *N*	0·37	0·031 g./10 c.c.	4·79
2·0	0·49	0·014	2·70
1·0	0·58	0·009	2·34
0·5	0·66	0·006	2·19
0·25	0·73	0·005	2·10
0·125	0·79	0·004	2·50
0·0625	0·85	0·004	2·50
0	—	0·003	—
			Mean 2·394

TABLE VII.

Formation of $(CH_3)_4NI_3$. Temp., 30°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln.	Equilib. const. *K*.
N/10	0·67	0·0026	—
N/20	0·72	0·0029	—
N/40	0·77	0·0046	10·98
N/60	0·79	0·0046	16·09
N/80	0·81	0·0044	15·59
N/100	0·82	0·0043	15·48
N/120	0·84	0·0042	15·39
N/160	0·85	0·0041	15·43
0	—	0·0038	—
			Mean 15·47

TABLE VIII.

Solubility of I_2 *in* $(C_2H_5)_4NI$. Temp., 25°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln
N/10	0·62	0·0027 g./10 c.c.
N/20	0·72	0·0028
N/100	0·80	0·0029
N/200	0·82	0·0031
N/500	0·84	0·0032
0	0	0·0038

TABLE IX.

Solubility of I_2 *in* $(C_2H_5)_4NBr$. Temp., 30°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln.
N/2	0·29	0·0018 g./10 c.c.
N/4	0·31	0·0021
N/8	0·33	0·0029
N/16	0·34	0·0033
N/32	0·35	0·0035
N/64	0·36	0·0036
0	—	0·0038

TABLE X.

Solubility of I_2 *in* $C_5H_5N{\cdot}C_2H_5I$. Temp., 30°.

Halide conc. ...	*N*/2	*N*/4	*N*/8	*N*/16	*N*/32	*N*/64	0
Solubility of I_2 in sat. soln. (g./10 c. c.). ...	0·0015	0·0016	0·0017	0·0017	0·0018	0·0027	0·0039

TABLE XI.

Formation of polyhalides of $(C_2H_5)_4NBr$. Temp., 30°.

Halide conc.	Degree of dissociation.	Solubility of Br_2 in sat. soln.	Equilib. const. *K* (calc. as Br_3).
N/2	0·29	0·28 g.	6·03
N/4	0·31	0·37	6·03
N/8	0·33	0·34	6·06
N/16	0·34	0·32	6·13
N/32	0·35	0·32	13·43
N/64	0·36	0·31	14·20
0	—	0·30	—
			Mean 6·08

TABLE XII.

Solubility of Br_2 *in* $C_5H_5N{\cdot}C_2H_5Br$. Temp., 25°.

Halide conc. ...	*N*/4	*N*/8	*N*/16	*N*/32	*N*/64	*N*/128	0
Solubility of Br_2 in sat. soln. (g./10 c.c.) ...	0·10	0·11	0·31	0·31	0·32	0·31	0·31

TABLE XIII.

Formation of $C_5H_5N{\cdot}C_2H_5BrI_2$. Temp., 30°.

Halide conc.	Degree of dissociation.	Solubility of I_2 in sat. soln.	Equilib. const. *K*.
N/2	0·82	0·0099 g./10 c.c.	3·90
N/4	0·84	0·0069	3·70
N/8	0·89	0·0055	3·71
N/16	0·91	0·0047	3·73
N/32	0·93	0·0043	3·72
N/64	0·94	0·0041	3·85
0	—	0·0038	—
			Mean 3·770

Degree of dissociation of $(C_2H_5)_4NBr$ and $C_5H_5N{\cdot}C_2H_5Br$ were determined experimentally from conductivity measurements; the results are given in Tables XIV and XV.

TABLE XIV.

Degree of dissociation of $(C_2H_5)_4NBr$. Temp., 25°.

Dilution.	Conductance specific.	Conductance equiv.	Degree of dissociation.
2,000	0·0186	36·32	0·29
4,000	0·0099	39·50	0·32
8,000	0·0052	41·76	0·34
16,000	0·0027	43·06	0·35
32,000	0·0014	43·87	0·35
64,000	0·0007	45·22	0·36
		123·70*	

* Calculated from the mobility of $(C_2H_5)_4N$ and Br-ions.

TABLE XV.

Degree of dissociation of $C_5H_5N{\cdot}C_2H_5Br$. Temp., 30°.

Dilution.	Conductance.		Degree of dissociation.
	sp.	equiv.	
2,000	0·0460	92·00	0·82
4,000	0·0235	95·10	0·85
8,000	0·0124	99·70	0·89
16,000	0·0064	103·00	0·92
32,000	0·0032	104·80	0·94
64,000	0·0016	106·10	0·95
128,000	0·0008	107·00	0·96
256,000	0·0004	109·40	0·98
		112·00*	

The compound $C_5H_5N{\cdot}C_2H_5Br$ was found to be extremely hygroscopic. In determining the specific conductance, every possible precaution was taken to dry the substance but the results obtained are not probably extremely accurate although sufficiently reliable for the present purpose.

From the preceding tables, it will be observed that the value of the equilibrium constant of the same complex ion varies with the nature of the cations as has already been pointed out (Ray, *loc. cit.*). Thus the present work also concords with the observation that the linkage between the halogen atoms of the complex is of an electrostatic nature (*cf.* Ray, *loc. cit.*).

The authors desire to express their thanks to Dr. P. Neogi for his kind interest in the work.

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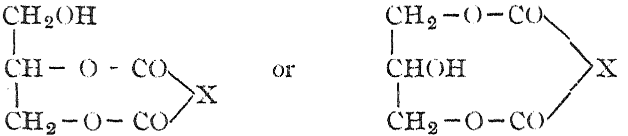
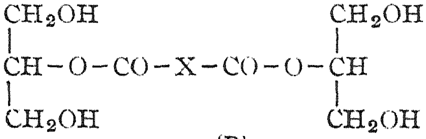
* Calculated by extrapolation.

Attempts to Prepare Ring Glycerides. Preparation of Tetrachlorodiglycerides of Dicarboxylic Acids

By M. Goswami and A. Shaha.

So far as our present knowledge of the constitution of fixed oils and fats goes the latter is universally based on the idea that only monocarboxylic fatty acids take part. There are, however, many fruits having pulp rich in dicarboxylic acids like malic and tartaric acids etc. A possibility, therefore, exists of the occurrence of glycerides of dicarboxylic acids in the seeds of those fruits, either in the ring form (A) or in the form (B) in which the dicarboxylic acid links up two glycerol molecules where X is a bivalent radical connecting two COOH group (this X is absent in the case of oxalic acid).


(A)

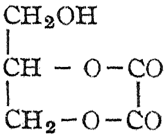


$$\begin{array}{lcl} CH_2OH & & CH_2OH \\ | & & | \\ CH-O-CO-X-CO-O- & & CH \\ | & & | \\ CH_2OH & & CH_2OH \end{array}$$

(B)

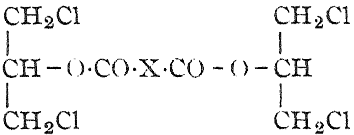
The form (B) has been shown to be $\beta\beta$-type but the possibility of having $\alpha\alpha$, $\alpha\beta$ or mixed type is not precluded.

Previous attempts to prepare glycerides of dicarboxylic acids have given inconclusive results. Thus Chattaway (*J. Chem. Soc.*, 1914, **105**, 151) after heating oxalic acid and glycerol for a short time at 50° and then keeping at room temperature for 3 months found diminished acid value from which and other reactions he concluded that combination had taken place to form (C) and an acid ester. He, however, did not


(C)

isolate any product. Kienle and Hovey (*J. Amer. Chem. Soc.*, 1929, 509) found only polymerised product from the interaction of glycerol and phthalic acid although he got indication of esterification at first.

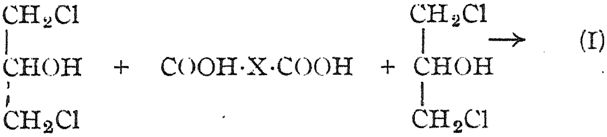
With a view to prepare the glycerides in question, a mixture of anhydrous glycerol and the dicarboxylic acid was heated in presence of phosphorus oxychloride. The product was washed with water and then treated with sodium bicarbonate, when a liquid remained. After repeated washing and then drying, the saponification values corresponded with those demanded by (A) or (B). Detection of elements, however, showed the presence of chlorine. The products were, therefore, distilled in vacuum. It was inferred from the M. W. determination, halogen estimation and the saponification values, that the glycerides obtained were of the following types



$$\begin{array}{lcl} CH_2Cl & & CH_2Cl \\ | & & | \\ CH-O\cdot CO\cdot X\cdot CO-O- & & CH \\ | & & | \\ CH_2Cl & & CH_2Cl \end{array}$$

(I)

The $\beta\beta$ linkage was confirmed by direct preparation of identical product from $\alpha\alpha$-dichlorohydrin and dicarboxylic acid thus :—



$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} + COOH\cdot X\cdot COOH + \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \rightarrow (I)$$

The following diglycerides have been prepared :

(*i*) Tetrachloro-$\beta\beta$-diglycerosuccinin (I, $X=CH_2\cdot CH_2$)
(*ii*) Tetrachloro-$\beta\beta$-diglyceromalein (I, $X=CH:CH$)
(*iii*) Tetrachloro-$\beta\beta$-diglycerocitraconin (I, $X=CMe:CH$)
(*iv*) Tetrachloro-$\beta\beta$-diglycerophthalein (I, $X=C_6H_4$)

Attempts are being made to prepare glycerides of the type (A) from $\alpha\beta$-dihalogenhydrins and silver and mercury salts of dicarboxylic acids. The results of these are reserved for future communication.

EXPERIMENTAL.

Tetrachloro-$\beta\beta$-diglycerosuccinin.—Succinic acid (12 g.) and anhydrous glycerol (18 g.) were heated on the sand-bath in a conical flask fitted with a reflux condenser (with a $CaCl_2$ tube at the top) and a dropping funnel until a homogeneous liquid was obtained. The flask was then removed from the source of heat and phosphorus oxychloride (30 c.c.) was added gradually from the dropping funnel. The reaction became very vigorous and gases were evolved. After the addition of phosphorus oxychloride the flask was heated on the water-bath until no more hydrochloric acid came out. The mixture was then allowed to cool and then treated with water when an emulsion occurred with a layer of oily liquid at the bottom. The whole was then kept overnight in contact with solid sodium bicarbonate. The oily layer was then extracted with ether and the ethereal solution was dried over P_2O_5. The ether was then driven off and the thick oil obtained was distilled at 141°-142°/4 mm., yield 4 g. (Found: Cl, 41·32; M. W., 333·3; sap. value, 980. $C_{10}H_{14}O_4Cl_4$ requires Cl, 41·76 per cent. M. W. 340; sap. value, 988·1).

Tetrachloro-ββ-diglyceromalein.—Maleic anhydride (19 g.) and anhydrous glycerol (37 g.) were treated as above with $POCl_3$ (40 c.c.). The purified product was distilled at 128-130°/4 mm., yield 9 g. (Found: Cl, 41·[illegible]; M. W., 336·7; sap. value, 984·9. $C_{10}H_{12}O_4Cl_4$ requires Cl, 42·01 per cent. M. W., 338; sap. value, 994).

Tetrachloro-ββ-diglycerocitraconin.—Citraconic anhydride (11 g.), anhydrous glycerol (18 g.) and $POCl_3$ (30 c.c.) were treated as above. The product was distilled at 228-232°/4 mm., yield 5 g. (Found: Cl, 39·95; M. W., 342·3; sap. value, 949·6. $C_{11}H_{14}O_4Cl_4$ requires Cl, 40·34 per cent. M. W., 352; sap. value, 954·8).

Tetrachloro-ββ-diglycerophthalein.—Phthalic anhydride (15 g.), anhydrous glycerol (18 g.) and $POCl_3$ (30 c.c.) were treated as above and the product distilled at 260-262°/4 mm., yield 7 g. (Found: Cl, 36·07 ; M. W., 382·8; sap. value, 853·9. $C_{14}H_{14}O_4Cl_4$ requires Cl, 36·79 per cent. M. W., 388; sap. value, 865).

Reaction Product from αα-Dichlorohydrin and Phthalic Anhydride.—αα-Dichlorohydrin (25 g.) and phthalic anhydride (7 g.) were treated with $POCl_3$ (20 c.c.) and the product was isolated as usual and distilled at 260-262°/4 mm. (Found: Cl, 36·25; M. W., 383 ; sap. value, 854·1.) The product was, therefore, considered to be identical with that obtained from phthalic anhydride and glycerol.

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The Rotatory Powers of Substituted Camphoranilic Acids.

BY MAHAN SINGH.

The present work is in continuation of the work already reported in a series of communications (*J. Chem. Soc.*, 1925, 1966; 1927, 1944; 1928, 2410 ; 1930, 1301; 1931,478; *J. Indian Chem. Soc.*, 1932, **9**, 363, 1934, **11**, 433). The following acids have now been prepared: 2′-and 4′-ethyl-, 3′-and 4′-fluoro-, 3′-and 4′-nitro-, 3′-and 4′-amino-, 3′-and 4′-acetylamino-, 3′-and 4′-acetyl-, 2′-nitro-4′ethyl-, 2′-nitro-3′-fluoro-, 2′-nitro-4′-fluoro-, 2′-nitro-4′-acetylcamphoranilic acids.

In the case of fluoro-, nitro-, amino-, acetylamino- and aceto-camphoranilic acids, the *para* isomeride has a greater rotatory power than the corresponding *meta* derivative. The rotatory powers of ethylcamphoranilic acids (Table I) are of the same order as those of the methylcamphoranilic acids.

TABLE I.

Solvent.	*o*-Me.	*p*-Me.	*o*-Et.	*p*-Et.
MeOH	151°	170°	153°	179°
EtOH	127	137	137	145
Me_2CO	98	122	117	102
MeEtCO	90	—	94	112

Table II gives the rotatory powers of *m*- and *p*-methyl and *m*- and *p*-acetocamphoranillc acids.

TABLE II.

Solvent.	*m*-Me.	*m*-COMe.	*p*-Me.	*p*-COMe.
MeOH	137°	118°	170°	214°
EtOH	121	99	137	215
Me_2CO	95	61	122	164
MeEtCO	108	71	—	161

The introduction of the carbonyl group caused an increase in the rotatory power of methylcamphoranilic acid. Rule and Smith (*J. Chem. Soc.*, 1926, 553) have also shown that the acetyl group, like other positive groups, produces an exaltation in the rotatory power. In the *meta* position, however, there is a fall in all the four solvents.

Table III records the rotatory powers of *meta*- and *para*- fluoro-, chloro-, bromo-, iodocamphoranilic acids in methyl alcohol and acetone.

TABLE III.

Solvent.	*m*-F.	*m*-Cl.	*m*-Br.	*m*-I.
MeOH	154°	162°	157°	167°
Me_2CO	104	97	111	119
	p-F.	*p*-Cl.	*p*-Br.	*p*-I.
MeOH	125	183	182	177
Me_2CO	54	119	125	146

The rotatory powers of *m*-fluoro acid are of the same order as those of the other *meta*- halogeno acids but in the *para*-fluoro acid there is a remarkable decrease particularly in acetone. It has not been possible to prepare *o*-fluorocamphoranilic acid and, therefore, the effect of the fluorine atom in the *ortho*-position has not been studied. It is, however, expected that it would give an abnormally low value.

The nitro group in the *meta*-position has a depressing effect. The rotatory power of *m*-nitrocamphoranilic acid is the lowest as shown in Table IV.

TABLE IV.

m-COOH.	*m*-Br.	*m*-OEt.	*m*-I.	*m*-OMe.	*m*-Cl.	*m*-F.	*m*-Me.	*m*-NO_2.
466°	182°	179°	177°	163°	162°	153°	140°	138°

The nitro group in the *para*-position produces a small increase in the rotatory power of camphoranilic acid. It has been mentioned before that this group in the *para*-position in disubstituted camphoranilic acids has a depressing effect. The nitro group is strongly polar and it was expected that *p*-nitrocamphoranilic acid would give values of the order of *p*-carboxycamphoranilic acid. This behaviour of the nitro group is, therefore, abnormal. The *m*-and *p*-nitrocamphoranilic acids have been reduced by ferrous sulphate and ammonia, the procedure given in literature being modified in minor details. The yield of the aminocamphoranilic acid is satisfactory but the purification is rather tedious. The amino groups are shown to have produced an exhaltation of rotation but not to the extent as was expected. This may be due to the presence of a carboxylic group in the molecule.

The acetylaminocamphoranilic acids were prepared by acetylating the above amino acids and also by condensing camphoric anhydride with *m*-and *p*-aminoacetanilides. They were shown to be identical by mixed melting point.

The rotatory powers of the free amino acids and the acetylated products are shown in Table V.

TABLE V.

Solvent.	*m*-NH_2.	*m*-NHCOMe.	*p*-NH_2	*p*-NHCOMe.
MeOH	134°	83·0°	166·8°	169·6°
EtOH	120	76·3	154·0	161·4
Me_2CO	124	56·0	—	141·0
MeEtCO	124·4	67·0	—	142·0

The *m*-acetylaminocamphoranilic acid has lower values than the *m*-amino acid in all the four solvents. The *p*-amino acid could only be examined in alcohols, because in the other two solvents it gave coloured solutions which could not be viewed clearly. In these solvents the values are slightly lower than the corresponding values of *p*-acetylaminocamphoranilic acid.

The following acids have been nitrated: 3′-fluoro-, 4′-fluoro, 4′-ethyl-, 4′-acetocamphoranilic acids. The nitration of 4′-chloro-, 4′-bromo-, 4′-methylcamphoranilic acids has been described by Singh and Singh (*J. Chem. Soc.*, 1931, 478). The rotatory powers of these nitro acids are shown in Table VI.

TABLE VI.

Acids.	MeOH.	EtOH.	Me_2CO.	MeEtCO.
4′-Fluoro-2′-nitro-	−45·0°	−49·6°	−47·6°	−47·5
4′-Chloro-2′-nitro-	−40·8	−51·8	−47·2	−35·2
4′-Bromo-2′-nitro-	−39·2	−45·3	−35·9	−31·5
4′-Methyl-2′-nitro-	−50·0	−60·5	−48·1	−41·2
4′-Ethyl-2′-nitro-	−62·1	−72·9	−67·3	−60·6

In every case the nitro group in the 2′-position depresses the rotatory power of the original compound and produces reversal in the sign of rotation.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Mono-substituted Amines.

Camphoric anhydride and different amines in equimolecular proportions were heated with a little fused sodium acetate for 3-4 hours in an oil-bath at 120-150° and the product extracted with a dilute solution of sodium hydroxide or ammonium hydroxide to remove any imide which might have been formed during the condensation. The filtrate was acidified with dilute acetic acid and the solid mass thus formed crystallised from dilute alcohol (animal charcoal).

o-Ethylcamphoranilic Acid crystallised from dilute alcohol as a white powder, darkening at 165° and melting at 171°. It is soluble in the usual organic solvents, but insoluble in water. (Found: N, 4·70; Equiv., 301. $C_{18}H_{25}O_3N$ requires N, 4·62 per cent. Equiv., 303).

p-Ethylcamphoranilic Acid crystallised from dilute alcohol as a white microcrystalline mass, softening at 200° and melting at 202-203°. It is soluble in the usual organic solvents but insoluble in water. (Found: N, 4·72; Equiv., 301·5. $C_{18}H_{25}O_3N$ requires N, 4·62 per cent. Equiv., 303).

m-*Acetocamphoranilic Acid* is a light brown fluffy mass, m.p. 189-90°. (Found: N, 4·54; Equiv., 315. $C_{18}H_{23}O_4N$ requires N, 4·41 per cent. Equiv., 317).

p-Acetocamphoranilic Acid crystallised from dilute alcohol as a white crystalline mass with a very slight yellow tinge, m.p. 224-25°. (Found: N, 4·53; Equiv., 316. $C_{18}H_{23}O_4N$ requires N, 4·41 per cent. Eqiv., 317).

m-*Nitrocamphoranilic Acid.*—Condensation temperature 140-150° for 4 hours, or 180° for 5-10 minutes. It is a light yellow crystalline mass, m.p. 210°. (Found: N, 8·89. $C_{16}H_{20}O_5N_2$ requires N, 8·75 per cent).

p-Nitrocamphoranilic Acid.—Condensation temperature 140-150° for 4 hours, but the yield was better at 180° for 5-10 minutes. It is a light yellow microcrystalline mass, m.p. 202-203°. It is soluble in the usual organic solvents, insoluble in water. (Found : N, 8·87. $C_{16}H_{20}O_5N_2$ requires N, 8·75 per cent).

Reduction of Nitrocamphoranilic Acids.

To a boiling solution of 36 g. of ferrous sulphate dissolved in a small quantity of water an ammoniacal solution of the acid (3 g.) was added in small quantities with continuous shaking. When the whole of the acid solution had been added, liquor ammonia was added until the colour of the reaction mixture became black. It was then concentrated and filtered and the filtrate acidified with acetic acid and the precipitate obtained on cooling was crystallised from dilute alcohol.

m-*Aminocamphoranilic Acid* crystallised from dilute alcohol as a white mass having a slight pinkish tinge, m.p. 196-97°. (Found : N, 9·85. Equiv., 291. $C_{16}H_{22}O_3N_2$ requires N, 9·65 per cent. Equiv., 290).

p-*Aminocamphoranilic Acid* could not be recrystallised from dilute alcohol as it decomposed on crystallisation. It was purified by repeated precipitation and dissolution. It was obtained as a fine pinkish powder, m.p. 220-21°. (Found : N, 9·76; Equiv., 289. $C_{16}H_{22}O_3N_2$ requires N, 9·65 per cent. Equiv., 290).

m-*Acetylaminocamphoranilic Acid.*—Temperature of condensation 140-150° for 4 hours. It is a white shining crystalline powder, m.p. 220-21°. (Found : N, 8·57; Equiv., 330. $C_{18}H_{24}O_4N_2$ requires N, 8·43 per cent. Equiv., 332).

p-*Acetylaminocamphoranilic Acid.*—Condensation temperature 170-180° for 4 hours. It crystallised from dilute alcohol as a white mass with a slight pinkish tinge darkening at 231-32° and melting at 234-35°. (Found : N, 8·52; Equiv., 330. $C_{18}H_{24}O_4N_2$ requires N, 8·43 per cent., Equiv., 332).

m-*Fluorocamphoranilic Acid.*—Condensation temperature 130-140° for 3 hours. It crystallised as white mica-like shining crystals, m.p. 197°. (Found : N, 4·85. Equiv., 290. $C_{16}H_{20}O_3NF$ requires N, 4·77 per cent. Equiv., 293).

p-*Fluorocamphoranilic Acid.*—Condensation temperature 180° for 5 minutes or 140° for 4 hours, but in the latter case some imide was formed. The substance could not be crystallised from any solvent, hence it was purified by repeated precipitation and dissolution, m.p. 180-81°. (Found : N, 4·86; Equiv., 291. $C_{16}H_{20}O_3NF$ requires N, 4·77 per cent. Equiv., 293).

Nitration.

The acid (3 g.) was added in small quantities at a time to a mixture of 10 c.c. of fuming nitric acid and 8 c.c. of glacial acetic acid cooled in ice and thoroughly shaken. The solution was cooled in ice for 45 minutes after which it was poured into ice. The precipitate was crystallised from dilute alcohol, yield theoretical.

2′-Nitro-4′-ethylcamphoranilic Acid crystallised from dilute alcohol in a fine yellow crystalline fluffy mass, m.p. 140·5°. (Found : N, 8·20. $C_{18}H_{24}O_5N_2$ requires N, 8·05 per cent).

2′-Nitro-3′-fluorocamphoranilic Acid separated from dilute alcohol as a yellow crystalline powder, m.p. 131-32°. (Found : N, 8·41. $C_{16}H_{19}O_5N_2F$ requires N, 8·28 per cent).

2′-Nitro-4′fluorocamphoranilic Acid separated from dilute alcohol as a fine dark yellow crystalline powder, m.p. 171°. It is soluble in organic solvents and insoluble in water. (Found : N, 8·44. $C_{16}H_{19}O_5N_2F$ requires N, 8·28 per cent).

2′-Nitro-4′-acetocamphoranilic Acid crystallised from dilute alcohol in yellow plates, m.p. 202-203°. (Found : N, 7·82. $C_{18}H_{24}O_6N_2$ requires N, 7·73 per cent).

o-*Ethylcamphorophenylimide.*—Temperature of condensation 180-200° for 4 hours. It crystallised from dilute alcohol as a white mass with a slight pinkish tinge, m.p. 132-33°. (Found : N, 5·0. $C_{18}H_{23}O_2N$ requires N, 4·91 per cent).

p-*Ethylcamphorophenylimide.*—Temperature of condensation was 200°. Slight traces of the acid were washed out with dilute ammonia. The insoluble imide was crystallised from dilute alcohol in white shining crystals, m.p. 123°. It is soluble in the usual organic solvents, insoluble in water. (Found : N, 4·97. $C_{18}H_{23}O_2N$ requires N, 4·91 per cent).

The rotations were determined by dissolving a known weight of the substance in a known volume of the solvent. The following results, without any mutarotation, were obtained. The length of the polarimeter tube was 2 dcm. in all cases. The temperature of the dark room varied between 17°-19°.

TABLE VII.

Solvent*	Conc.	$[\alpha]$.	$[\alpha]_D$.	Conc.	$[\alpha]$.	$[\alpha]_D$.
	o-Ethyl-				p-Ethyl-	
A	0·2000 g./25 c.c.	0·81	50·6	0·2027 g./25 c.c.	0·96	59·2

TABLE VII. (contd.)

Solvent.	Conc.	$[\alpha]$.	$[\alpha]_D$.	Conc.	$[\alpha]$.	$[\alpha]_D$.
	o-Ethyl-			*p*-Ethyl-		
B	0·2179 g./25 c.c.	0·79	45·3	0·2035 g./25 c.c.	0·78	47·9
C	0·2002	0·50	31·2	0·2027	0·60	37·0
D	0·2032	0·63	38·8	0·2070	0·56	33·8
	m-Aceto-			*p*-Aceto-		
A	0·2000	0·59	36·9	0·2018	1·09	67·5
B	0·2025	0·50	30·9	0·2013	1·09	67·7
C	0·2001	0·31	19·4	0·2004	0·83	51·8
D	0·2034	0·33	20·3	0·2041	0·83	50·8
	m-Nitro-			*p*-Nitro-		
A	0·2055	0·71	43·2	0·2000	1·21	75·6
B	0·2025	0·55	34·0	0·2088	1·19	71·2
C	0·2008	0·41	25·5	0·2029	0·92	56·6
D	0·2020	0·45	27·8	0·2002	1·03	64·3
	m-Amino-			*p*-Amino-		
A	0·2000	0·74	46·3	0·1000	0·46	57·5
B	0·2008	0·67	41·7	0·2000	0·85	53·1
C	0·1924	0·66	42·8			
D	0·1969	0·66	42·9			
	m-Acetylamino-			*p*-Acetylamino-		
A	0·2000	0·40	25·0	0·2006	0·82	51·1
B	0·2012	0·37	23·0	0·1980	0·77	48·6
C	0·2069	0·28	16·9	0·2002	0·68	42·5
D	0·2042	0·33	20·2	0·2014	0·69	42·8

* A = Methyl alcohol; B = Acetone; C = Ethyl alcohol;
D = Methylethyl ketone.

TABLE VII. (contd.).

Solvent.	Conc.	$[\alpha]$.	$[\alpha]_D$.	Conc.	$[\alpha]$.	$[\alpha]_D$.
	m-Fluoro-			*p*-Fluoro-		
A	0·2005	0·84	52·4	0·2047	0·70	42·7
B	0·2038	0·66	40·5	0·2044	0·67	41·0
C	0·2012	0·57	35·4	0·2024	0·30	18·5
D	0·2007	0·54	33·6	0·2100	0·44	26.2
	2′-Nitro-4′-ethyl-			2′-Nitro-3′-fluoro-		
A	0·2012 g./25 c.c.	−1·00	−62·1	0·2000 g./25 c.c.	−0·23	−14·4
B	0·2023	−1·18	−72·9	0·2000	−0·40	−25·0
C	0·2005	−1·08	−67·3	0·2000	−0·31	−19·4
D	0·2002	−0·97	−60·6	0·2000	−0·17	−10·6
	2′-Nitro-4′-fluoro-			2′-Nitro-4′-aceto-		
A	0·2000	−0·72	−45·0	0·2003	0·83	51·8
B	0·2066	−0·82	−49·6	0·2000	0·71	44·4
C	0·2100	−0·80	−47·6	0·2001	0·67	41·8
D	0·2000	−0·76	−47·5	0·2002	0·63	39·3
	o-Ethylcamphorophenylimide			*p*-Ethylcamphorophenylimide		
A	0·4008	0·63	19·6	0·4005	0·51	15·9
B	0·3945	0·62	19·7	0·4910	0·57	14·5
C	0·3996	0·51	16·0	0·4000	0·51	15·9
D	0·3952	0·50	15·8	0·4002	0·43	13·4

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Chloral Derivatives of Salicylic Acid.

By Narshinh Muljibhai Shah and Rupchand
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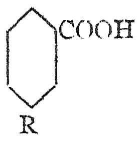
During the course of their work on chlorides (*J. Indian Chem. Soc.*, 1934, **11**, 545) the present authors tried to prepare the salicylic acid chloralide. The condensation was tried under varying conditions: (*a*) Wallach's method (*Annalen*, 1878, **193**, 1), was repeated to no advantage; (*b*) the condensation was repeated in presence of different condensing agents, *viz.*, glacial acetic acid, concentrated hydrochloric acid and sulphuric acid; acetic acid and hydrochloric acid did not effect the condensation, while sulphuric acid gave a product from which no crystalline substance could be separated (*cf.* Chattaway and Calvet, *J. Chem. Soc.*, 1928, 1090).

The present authors, thinking that this complexity was due to the activity of OH-group in the salicylic acid, decided to study the condensation with the methyl ether of salicylic acid. After this work on methyl ether derivatives had proceeded, our attention was drawn to a paper by Hurry and Meldrum (*J. Indian Chem. Soc.*, 1934, **11**, 535) on some derivatives of *o*-methoxybenzoic acid along similar lines. This rendered much of our work superfluous and although we confirm their results in general, the results obtained so far are interesting enough for publication.

It is found that in addition to the product (I, $R=CHOH\cdot CCl_3$) there is present in the sulphuric acid filtrate a sulphonic acid, which is easily converted into it on boiling. This accounts for the low yield of (I, $R=CHOH\cdot CCl_3$) obtained by Hurry and Meldrum (*loc. cit.*). Generally the products obtained by Hurry and Meldrum are not well purified; this can be seen from the following table.



(I)

Substance.	Hurry and Meldrum (m.p.).	Shah and Alimchandani (m.p.).
Condensation product (I, $R=CHOH{\cdot}CCl_3$)	216°	224°
Reduction product (I, $R=CH_2CHCl_2$)	127°	134-35°
Tetrachloro product (I, $R=CHCl{\cdot}CCl_3$)	132°	138°

The action of bromine and of dry HCl as described by Yelburgi and Wheeler (*J. Indian Chem. Soc.*, 1934, **11**, 217) was tried on the reduction product (I, $R=CH_2{\cdot}CHCl_2$) with no effect. This proves that it has the saturated formula containing the group CH_2CHCl_2. The reduction product (I, $R=CH_2CHCl_2$) on treatment with concentrated H_2SO_4 gave 4-methoxy-5-carboxyphenylacetic acid (I, $R=CH_2{\cdot}COOH$). The condensation product (I, $R=CHOH{\cdot}CCl_3$) was treated with sulphuric acid. A yellow mass was obtained from which two products were separated: (*a*) colourless crystals, m.p. 138°, found to be identical with Hurry and Meldrum's 5-carboxy-4-methoxy-1-$\alpha\beta\beta\beta$-tetrachloroethylbenzene (I, $R=CHCl{\cdot}CCl_3$) and (*b*) a substance in a very small quantity, m.p. 177°, which could not be investigated further.

The above condensation of chloral, however, excludes the possibility of the chloralide formation. The reactivity of the free acid may perhaps be moderated by the introduction of suitable substituents in the nucleus. With this end in view, we studied the condensation with 3-nitro-and 5-nitrosalicylic acids and their methyl ethers (*Current Science,* 1935, **3**, 354). We then tried to condense chloral with 3-amino-, 5-amino-, 5-sulpho-, and 5-bromosalicylic acids by different methods. In all these cases, the condensation could not be effected. Details of these unsuccessful attempts to condense chloral with the substituted salicylic acids are omitted from the experimental part.

EXPERIMENTAL.

Salicylic acid has been methylated according to the method of Meldrum and Shah (*J. Chem. Soc.*, 1923, **123**, 1987). The methoxy acid after recrystallisation from a mixture of chloroform and petroleum ether melts at 106° (Meldrum and Shah, m.p. 100·5°).

4-Methoxy-5-carboxy-1-α-hydroxy-βββ-trichloroethylbenzene (I, $R=CHOH{\cdot}CCl_3$).—Finely powdered methoxysalicylic acid (10 g.), chloral hydrate (12 g.) and concentrated sulphuric acid (30 c.c.) were mixed and the clear solution after keeping for 5 days was poured into ice, when a pasty mass separated which solidified on washing with water. It crystallised from boiling glacial acetic acid in small needles;

recrystallised from ethyl acetate, m.p. 224°. (Found : Cl, 35·44. Calc. for $C_{10}H_9O_4Cl_3$: Cl, 35·54 per cent).

The sulphuric acid filtrate was evaporated in an air-oven when white crystals began to separate, which were found to be identical with the condensation product, total yield 9 g.

Reduction product (I, $R=CH_2{\cdot}CHCl_2$).—To the hot solution of the above substance (5 g.) in acetic acid (25 c.c.), zinc dust (4 g.) was gradually added in small amount and the mixture was filtered from unchanged zinc and the filtrate diluted with water, when a white light substance came down. It was first crystallised from acetic acid and then from benzene, m.p. 134-35°, yield almost theoretical. (Found : C, 48·22; H, 3·63 ; Cl, 28·35. Calc. for $C_{10}H_{10}O_3Cl_2$: C, 48·2; H, 4·01 ; Cl, 28·5 per cent).

4-Methoxy-5-carboxyphenylacetic Acid (I, $R=CH_2{\cdot}COOH$).—The reduction product (5 g.) was heated with concentrated sulphuric acid (25 c.c.) on a water-bath when HCl gas was evolved. After the reaction was over, the mixture was poured into ice-cold water when the crystals slowly separated. It crystallised from water with 1 H_2O, m.p. 141-42°. (Found : H_2O, 7·7 ; Equiv., 114·3. $C_{10}H_{10}O_5$, $1H_2O$ requires H_2O, 7·89 per cent. Equiv., 114). It crystallised from a mixture of acetone and benzene as clusters of long silky needles, m.p. 153°. (Found : Equiv., 105·5. $C_{10}H_{10}O_5$ requires Equiv., 105).

Action of Sulphuric acid on the substance (I, $R=CHOH{\cdot}CCl_3$).—The substance (1 g.) was dissolved in concentrated sulphuric acid (25 c.c.) and heated on a water-bath for about an hour. Effervesence of HCl gas began at about 75° and the colour of the solution turned brown. After the reaction was over, the mixture was cooled and poured into cold water when a yellow pasty mass separated which slowly solidified on washing with water. On crystallising from a mixture of benzene and petroleum ether and then from ethyl acetate, two types of crystals were observed : (*i*) colourless prismatic, m.p. 135°; (*ii*) deep yellow, m.p. 170°. The prismatic crystals on further recrystallisation from acetic acid melted at 138°. This was found to be identical with Hurry and Meldrum's tetrachloro derivative (I, $CHCl{\cdot}CCl_3$). From deep yellow material, a very small quantity of a coloured product, m.p. 177°, was obtained which could not be further investigated.

We are thankful to Mr. H. V. Dharwarkar for his help in carrying out some of the experimental work.

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Methoxy-oxypalmatine.

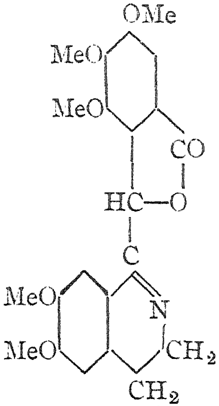
By Narindra Nath Chopra and Jnanendra Nath Rây.

Späth and Bohm (*Ber.*, 1922, **55**, 2985 and subsequent papers) reinvestigated Columba roots and isolated a substance which was chemically and crystallographically identical with palmatine. Hence they concluded that columbamine of Feist (*Arch. Pharm.*, 1907, **245**, 586) is an impure specimen of palmatine, a view with which Feist seems to have agreed. By the oxidation of columbamine Feist (*loc. cit.*) obtained corydaldine and an acid which he regarded as trimethoxyphthalic acid. The constitution of this acid has been the subject matter of numerous investigations, but unanimity has not yet been reached with regard to its physical constants (*cf.* Herzig, *Annalen*, 1920, **421**, 287).

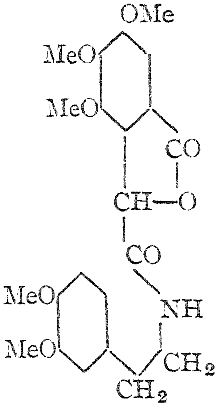
3:4:5-Trimethoxy-*o*-phthalic acid has been obtained by the oxidation of colchicine by Windaus (*Sitzungsber. Hiedelberger Akad. Wiss.*, 1910, 1; 1911, 1). We are synthesising this acid by a new method, the details of which will be published later on. If columbamine is identical with palmatine, Feist's acid can be either *m*-hemipinic acid or hemipinic acid.

Späth and Bohm (*loc. cit.*) attempted the synthesis of tetrahydrocolumbamine (methoxytetrahydropalmatine) by condensing 6:7-dimethoxy-1-(3′:4′:5′-trimethoxy) benzyl-1:2:3:4-tetrahydro*iso*quinoline and methylal. Amorphous products were obtained which consisted largely of the condensation product of two molecules of the *iso*quinoline with one of methylal. It has been claimed that by regulating the proportions of the reactants an amorphous base of the tetrahydroberberine type can also be obtained. But no attempt seems to have been made to isolate it in a pure condition.

We have now obtained the substance (I) by ring-closure of the amide (II), obtained from the chloride of 3:4:5-trimethoxyphthalidecarboxylic acid, and 3:5-dimethoxyphenylethylamine, by the Bischler-Napieralsky reaction. This has been converted into (III) by following a scheme analogous to Perkin, Rây and Robinson's oxyberberine synthesis (*J. Chem. Soc.*, 1925, **127**, 740).

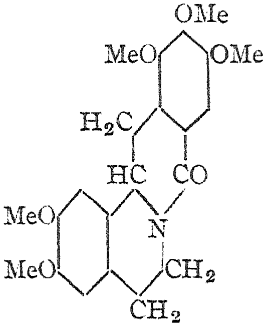


(I)



(II)

But when β-2:3:4-trimethoxyphenylethylamide of meconine carboxylic acid (IV) was subjected to Bischler-Napieralsky reaction no *iso*quinoline was formed in an appreciable amount. At any rate, we could not isolate any crystalline product from the reaction. It seems there is very little activation of the nuclear hydrogen atom marked (*) for ring closure. In view of this, we do not feel surprised that Späth and Bohm (*loc. cit.*) could not isolate their base of the tetrahydro berberine type in a pure condition.



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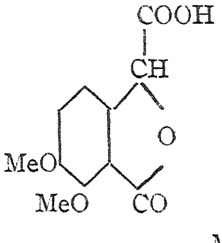

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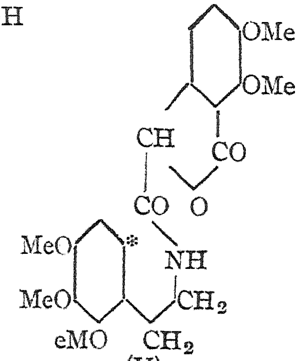

(V)

E X P E R I M E N T A L.

β-3:4-*Dimethoxyphenylethylamine.*—For this preparation the prescription of Ray (*J. Indian Chem. Soc.*, 1927, **4**, 403) was followed. The modification of Pyman (*J. Chem. Soc.*, 1929, 2014) results in the improvement of the yield of 3:4-dimethoxyphenylpropionamide by about 4% but involves much longer time.

3:4:5-*Trimethoxyphthalide carboxylic Acid.*—The demethylation observed by Alimchandani and Meldrum (*J. Chem. Soc.*, 1920, **117**, 964) can be avoided under the following circumstances:

Finely powdered gallic acid trimethyl ether (8 g.) was added in small portions and with vigorous shaking to an ice-cold solution of chloral hydrate (9 g.) in sulphuric acid (*d* 1·84, 50 c.c.), the temperature being maintained below 5° during addition. The mixture was left aside for 48 hours at 15-20° and then poured on to crushed ice. The precipitated trichlorophthalide was collected and extracted with boiling methyl alcohol, some bye-product remaining insoluble. On dilution with water, the methyl alcohol filtrate deposited an oil which was separated and hydrolysed with sodium hydroxide (15 g.) in water (120 c.c.) by boiling till a complete solution resulted. The well cooled solution was acidified with hydrochloric acid and then kept at 70-80° for 10 minutes, when on cooling the phthalide carboxylic acid separated in colourless needles, yield 7 g. The substance crystallises from water with a molecule of water of crystallisation, m.p. (after drying), 147°. (Found: C, 53·54; H, 4·68. $C_{12}H_{12}O_7$ requires C, 53·64; H, 4·92 per cent).

The Amide (II).—3:4:5-Trimethoxyphthalide carboxylic acid (2 g.) dissolved in dry benzene was treated with thionyl chloride (4 c.c.) and the mixture kept at 50-60° for ½ hour. After removal of the volatile matter in *vacuo*, the residue was treated with fresh benzene and the solvent again removed in *vacuo*. Finally the residue was heated at 100° for a few minutes in *vacuo* and then dissolved in benzene (10 c.c.). The solution of the acid chloride was mixed with a solution of *β*-3:4-dimethoxyphenylethylamine (1·3 g.) and pyridine (0·6 g.) in dry benzene (10 c.c.) with cooling and left aside for 2 hours. After washing successively with water, dilute hydrochloric acid, dilute ammonia and again with water, the solvent was removed from the benzene layer. The residue crystallised from alcohol in plates, m.p. 154°, yield 2 g. (Found: N, 3·4. $C_{22}H_{25}O_8N$ requires N, 3·25 per cent).

The iso*Quinoline* (I).—The foregoing amide (2 g.) in phosphoryl chloride (20 c.c.) was very gently heated on the steam-bath for 5 hours. The temperature of the reaction mixture was not allowed to rise above 60°. The solution was decomposed with crushed ice and left aside for ½ hour and then filtered from a tarry impurity. The well cooled bright yellow filtrate was basified below 10°. The ochreous yellow precipitate was well washed, dried in *vacuo* over sodium hydroxide and then dissolved in ethyl acetate. The residual *iso*quinoline from the filtered ethyl acetate solution was used directly for conversion into the methoxyoxypalmatine (III), yield 40%.

Methoxy-oxypalmatine (III).—The crude *iso*quinoline, obtained above, was reduced with zinc dust (7 g.) added in small amounts in glacial acetic acid solution by boiling for about 10 minutes. The reduction of the dihydro*iso*quinoline to the tetrahydro stage was accompanied by a change of colour from brown to pale yellow, a bluish green fluorescence developing. The solution filtered from zinc dust was diluted with ethyl acetate and the solution washed well with water to remove acetic acid and then the solvent removed from the ethyl acetate layer. The oily residue was dissolved in alcohol (10 c.c.) and treated with sodium hydroxide (2 g.) in water (4 c.c.) and the mixture warmed on the steam-bath for 5 minutes. On pouring into water (150 c.c.) methoxy-oxypalmatine was precipitated in a crystalline form. Recrystallised from hot aqueous alcohol it had m.p. 170°. (Found: C, 66·01 ; H, 6·07. $C_{22}H_{25}O_6N$ requires C, 66·16 ; H, 6·26 per cent .

A solution of the substance in neutral solvents has a pale yellow colour with a strong greenish blue fluorescence. A solution in 50% sulphuric acid gives with a drop of nitric acid a permanganate-violet colour which is discharged on dilution.

β-2 : 3 : 4-Trimethoxyphenylethylamine was prepared according to the method of Slottar and Heller (*Ber*., 1930, **63**, 3040) but we are unable to confirm the statement that the action of sodium hypochlorite on *β*-2 : 3 : 4-trimethoxyphenylpropionamide results in the production of a horny mass.

Trimethoxyphenylpropionamide (10 g.) was added in small portions to a solution of sodium hypochlorite, prepared with chlorine generated from potassium permanganate (3·5 g.) and hydrochloric acid (excess) and absorbed in 110 c.c. of 10% sodium hydroxide solution at 0°. After the whole of the amide had passed into solution the mixture was heated at 70° for 1 hour. It was then hydrolysed with sodium hydroxide (40 g.) at 70-80°. The liberated amine was extracted with benzene, dried and solvent removed. The crude amine was converted into the hydrochloride or the oxalate, m.p. 185°, after crystallisation from alcohol. (Found : N, 4·62. $C_{13}H_{19}O_7N$ requires N, 4·65 per cent).

The *β*-2 : 3 : 4-trimethoxyphenylethylamide of meconine carboxylic acid, prepared in the usual manner, gave very minute trace of an uncrystallisable basic material which resisted purification.

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LAHORE.

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Studies in the Acenaphthenequinone Series. Part II.

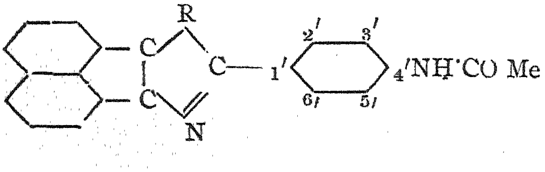
By ANUKUL CHANDRA SIRCAR AND SAILESH CHANDRA SEN.

The present investigation is a continuation of the work of Sircar and Sen (*J. Indian Chem. Soc.*, 1931, **8** 605) and undertaken with the object of establishing the formation of iminazoles from oxazoles, contrary to the work of Japp and co-workers (*J. Chem. Soc.*, 1882, **41**, 146).

Sircar and Sen (*loc. cit.*) have prepared both oxazoles and iminazoles from acenaphthenequinone in presence of ammonia with the same aldehyde under different experimental conditions; at the temperature of melting ice only oxazoles are formed while at higher temperature only iminazoles are formed. Again some of the aldehydes yielded a mixture of oxazole and iminazole at the temperature of melting ice.

The formation of both oxazoles and iminazoles by the condensation of the same aldehyde with acenaphthenequinone in presence of ammonia naturally leads one to suppose that probably in these reactions oxazoles are first formed which by subsequent replacement of the oxygen atom of the ring by the NH-group forms iminazoles. Ruhemann (*J. Chem. Soc.*, 1899, **75**, 713) and Meyer and Oppelt (*Ber.*, 1888, **21**, 3376) have actually been able to replace the oxygen atom by NH-group in pyrone and allied compounds. In order to justify the above supposition Sircar and Sen (*loc. cit.*) have shown that when an oxazole is heated with ammonia in a sealed tube under pressure, the percentage of nitrogen in the resulting product appreciably increased though the corresponding iminazole could not be isolated.

The authors have now been able to prepare 4′-acetylamino-2-phenylacenaphthiminazole (I, R = NH) from 4′-acetylamino-2-phenylacenaphthoxazole (I, R = O).



EXPERIMENTAL.

Acenaphthenequinone (1 g.) was thoroughly mixed with a little more than the molecular proportion of *p*-acetylaminobenzaldehyde, dissolved in boiling amyl alcohol, and dry ammonia gas was passed through the hot solution for about 4 minutes. When the reaction had just started, the mixture was cooled in a freezing mixture and ammonia gas was passed for 2 hours. A portion of it was allowed to stand overnight for the preparation of oxazoles and this oxazole had the same properties as described by Sircar and Sen (*loc. cit*). (Found : N, 8·81. Calc. for $C_{21}H_{14}O_2N_2$: N, 8·59 per cent). The solution left in the flask, was boiled and ammonia gas was passed through it for a further period of 2 hours and the solution left overnight. The separated red precipitate was washed with ether, crystallised from a mixture of alcohol and benzene as yellow microcrystalline powder, melting at 250° (decomp.) and had the properties of the iminazole as shown in our previous work. (Found : N, 12·60. Calc. for $C_{21}H_{15}ON_3$: N, 12·92 per cent). Similar results were, however, not obtained with other aldehydes.

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Parachor and the Structure of Formic Acid.

SUSIL KUMAR RAY.

Various structures have been proposed from time to time by different investigators for formic acid and the formates. Recently a paper has been published (Halasyam, *J. Indian Chem. Soc.*, 1935, **12**, 813) in which the structure of formic acid as proposed by Ray and Sarkar (*Proc. Indian Science Congress*, 1935, p. 109; *cf.* also Ray, *Nature*, 1934, **133**, 646) was supported by Halasyam from the standpoint of the parachor evidence. The object of the present paper is to analyse the arguments of Halasyam and to propose a structure for formic acid from the parachor evidence.

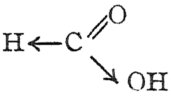
In calculating the theoretical parachor of formic acid, Halasyam adopted the values of Mumford and Phillips for the atomic and the structural constants on the plea that these are improvements on the older values of Sugden. The Mumford and Phillip's method of treating the parachor appears to possess no particular advantage over the system of Sugden and its application appears to be much more complicated. Although it is very probable that Sugden's parachor values may have to be modified in the future, and that further structural equivalents may need to be introduced, there is no doubt that this method of calculating parachors is so simple and the results it has already given are so useful that there appears to be particularly no advantage in replacing it by Mumford and Phillip's system. Moreover in order to prevent confusions and complications, it is better to have a standard, instead of having two different sets of constants. The present author is of opinion that so long as far more convincing results are not obtained by the new system, the use of Sugden's system must be retained, which appears to be the opinion of the majority of the investigators working in this direction. Halasyam has also neglected the very important factor, when adducing the parachor evidence for the structure of formic acid, that the molecules of formic acid are slightly associated. Thus it is apparent that the proof given by Halasyam from the parachor evidence, in support of the structure of formic acid, as suggested by Ray and Sarkar, has practically no weight.

In the present paper the surface tension and density of formic acid (Kahlbaum's extra-pure reagent further purified by repeated distillation) were determined at different temperatures and the parachors calculated. It will be observed from the results given in the following table that the parachor increases as the temperature is increased indicating that the molecules are associated to a slight extent (*cf.* Sugden, "The Parachor and Valency", 1930, p. 165). The value at 100° (*i.e.*, 95·5) has been obtained from the graph drawn by plotting the parachor against the respective temperature, and it may be assumed, without much errror, that the molecules exist mainly in the non-associated state at this temperature, (the b. p.) and that the value 95·5 thus obtained is the correct value of the non-associated formic acid molecule.

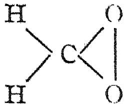
TABLE I.

Temp.	Density.	Surface tension.	Parachor.
0°	1·245	40·38	93·70
30	1·208	37·18	94·04
50	1·181	34·65	94·48
75	1·153	32·18	94·97
100	—	—	(95·50)

The calculated value for the structure proposed by Ray and Sarkar,



is 99·0, on the Sugden system. The difference between the theoretical value and the value at 100°, *i.e.*, 3·5 units is much greater than the experimental error. The only reasonable structure consistent with the observed parachor appears to be the following :



($P_{cal} = 95·7$)

However it must be admitted that in this case any particular structure can not be accepted simply from the parachor evidence, as the difference in the parachor value between the possible structures are not sufficiently large to arrive at a definite conclusion.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

Received April 8, 1936.

A Note on the Use of Adsorption Indicators in Acidimetry and Alkalimetry.

BY SACHINDRA NATH ROY.

So far, no investigation appears to have been made in order to find out the applicability of adsorption indicators in acidimetry and alkalimetry. In the present paper attempts have been made to describe a process in which adsorption indicators may be utilised in acidimetry and alkalimetry.

A known volume of standard nitric acid (not less than $N/20$) was taken in a conical flask and a few drops of fluorescein (0·50% soln. of sodium fluoresceinate) and 1 c. c. of 0·5% lead nitrate (approx. $N/30$) solution was added to it and the mixture titrated with caustic soda; the presence of small amounts of sodium carbonate was found to have no effect on the accuracy of the colour reaction. At a certain point the dull-green colour of the solution changes to a brilliant fluorescent green. The addition of alkali was continued in drops. The end-point was ascertained by the sudden disappearance of the fluorescent green colour and consequent development of a distinct yellow colour. The solution becomes turbid at the same time. The solution should be well shaken after the addition of each drop. It is always advisable to add a drop more to ensure the colour change. The colour change is sufficiently delicate to be distinguished even with $N/40$ solutions.

Eosin may be used instead of fluorescein, in which case the colour changes from red fluorescence to a brilliant turbid pink.

The strengths of alkali and acid (nitric acid) determined in this way were compared with those obtained by titration with methyl orange as indicator and the two results were found to be concordant. Hydrochloric and sulphuric acids cannot be estimated in this way as lead chloride and lead sulphate are precipitated.

Acetic acid also may be determined by this way. In this case the fluorescent colour appears much earlier than in the case of nitric acid. This is due to the hydrolysis of sodium acetate formed. But the colour change to yellow is not affected by it, unless the solutions are concentrated. For the colour reaction depends on the minimum p_H value, at which lead hydroxide may be formed and not on the p_H value of the solution, at which fluorescein assumes its alkaline colour.

The mechanism of the reaction is explained in the following way:—

As soon as the acid is neutralised, the extra drop of alkali reacts with lead nitrate forming lead hydroxide, on which are adsorbed lead and fluorescein ions giving rise to the characteristic red coloured dye-precipitate complex observed by Wellings (*Analyst*, 1933, **58**, 331).

The best results are obtained with *N*/10 to *N*/15 solutions. Large excesses of neutral salts affect the colour change to a considerable degree.

My thanks are due to Prof. A. Maitra for the kind interest he took in this work.

Received May 25, 1936.

Chemical Laboratory,
Presidency College,
Calcutta.

A Note on the Use of Adsorption Indicators in Acidimetry and Alkalimetry.

By Sachindra Nath Roy.

So far, no investigation appears to have been made in order to find out the applicability of adsorption indicators in acidimetry and alkalimetry. In the present paper attempts have been made to describe a process in which adsorption indicators may be utilised in acidimetry and alkalimetry.

A known volume of standard nitric acid (not less than $N/20$) was taken in a conical flask and a few drops of fluorescein (0·50% soln. of sodium fluoresceinate) and 1 c. c. of 0·5% lead nitrate (approx. $N/30$) solution was added to it and the mixture titrated with caustic soda; the presence of small amounts of sodium carbonate was found to have no effect on the accuracy of the colour reaction. At a certain point the dull-green colour of the solution changes to a brilliant fluorescent green. The addition of alkali was continued in drops. The end-point was ascertained by the sudden disappearance of the fluorescent green colour and consequent development of a distinct yellow colour. The solution becomes turbid at the same time. The solution should be well shaken after the addition of each drop. It is always advisable to add a drop more to ensure the colour change. The colour change is sufficiently delicate to be distinguished even with $N/40$ solutions.

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PAGE.				
451	Line 17*	*Read*	value	for volume
454	Fig. 1	,,	pH 6·5, 7·5, 8·5, 9·5,	for 5·5, 6·5 etc.
460	Table VI	,,	NH_4 FI_2	for NH_4 Et_2

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* From bottom.

A Magnetic Study of Colour Changes in Cobalt Chloride. Part II.

By S. S. Bhatnagar, A. N. Kapur and P. L. Kapur.

The changes in the colour of solution of cobaltous chloride were first observed by Hellot (*Mem. Acad.*, 1737, **101**, 228), Macquer ("Dictionnaire de Chimie, Neuchatel, 1789) and Proust (*J. Phys.*, 1806, **63**, 364, 421). Since then these colour changes red $\rightleftharpoons$ blue of cobaltous chloride solutions have continued to excite interest as is shown by the voluminous literature published on the subject.

One of the earliest attempts made to explain these colour changes was to assume that the red colour is due to the existence of the hexahydrate in solution and that the blue colour is due to the formation of a lower hydrate. The hydration hypothesis as put forward, by several scientists,* though plausible, does not explain all the phenomena, as for example, the different effects produced by anhydrous calcium and zinc chlorides. This led Engel (*Bull. Soc. chim.*, 1888, *ii*, **50**, 98; 1891, *iii*, **6**, 240) to elaborate a molecular compound hypothesis. Engel assumed that the various colours are produced by the presence of double salts in solution. The hypothesis fits in with some of the facts but needs too many unproved subsidiary hypotheses to be satisfactory. Donnan and Bassett (*J. Chem. Soc.*, 1902, **81**, 939) suggested an explanation based on the formation of complex ions. The complex-ion hypothesis assumes that in addition to the simple $Co^{\cdot\cdot}$-ions and Cl'-ions, there are also complex anions, e g., $CoCl_3{}'$ and $CoCl_4{}''$ in equilibrium, such that the simple process of ionisation

$$CoCl_2 \rightleftharpoons Co^{\cdot\cdot} + 2Cl'$$

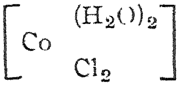
---

* Von Babo (*Ber. Verh. Naturforsch. Ges. Freiburg*, 1858, **1**, 277), Benrath (*Z. anorg. Chem.*, 1907, **54**, 328), Berthelot ("Thermochimie" Paris, 1897, **2**, 298), Brown (*Proc. Roy. Soc. Edin.*, 1912, **32**, 50; 1912, **33**, 44), Hartley (*Trans. Roy. Soc. Dublin*, 1900, *ii*, **7**, 253; *Proc. Chem. Soc.*, 1903, **19**, 49) and Moore (*Z. physikal. Chem.*, 1906, **55**, 641).

is followed by

$$CoCl_2 + 2Cl' \rightleftharpoons CoCl_4, \text{ or } CoCl_2 + Cl' \rightleftharpoons CoCl'_3$$

The non-ionised salt in solution is supposed to be blue, and the complex anion in solution is also blue, while the colour due to the cobalt atom when outside the immediate sphere of chlorine atoms, appears to be red. The different effects produced by anhydrous zinc and calcium chloride are explained on the fact that zinc having greater tendency to enter into negative complex groups, would form Co-$(ZnCl_4)$, while the calcium double chloride will have the constitution $Ca(CoCl_4)$, since cobalt has a greater tendency to form negative complexes than calcium. The work of Denham and co-workers (*Z. physikal. Chem.*, 1909, **65**, 641 ; *J. Amer. Chem. Soc.*, 1923, **45**, 1353) on transport numbers, of Moore (*Z. physikal. Chem.*, 1906, **55**, 641), Job (*Compt. rend.*, 1933, **196**, 181 ; 1934, **198**, 827), Groh and Schmidt (*Z. anorg. Chem.*, 1927, **162**, 321) on absorption spectra and of Bessett and Croucher (*J. Chem. Soc.*, 1930, 1784), on the equilibria of the complex salt of cobalt chloride with hydrochloric acid and mercuric, magnesium and zinc chlorides, favours the complex-ion hypothesis. Kotschubei (*J. Russ. Phys.-Chem. Soc.*, 1914, **46**, 1055) attributed the change in colour, not to the formation of $CoCl_4'$, but to the transition from the $Co(H_2O)_6^{\cdot\cdot}$-ion to the $Co(H_2O)^{\cdot\cdot}$-ion to



$$\left[\mathrm{Co}\begin{matrix}(H_2O)_2\\ Cl_2\end{matrix}\right].$$

Bhatnagar and Kapur (*J. Indian Chem. Soc.*, 1932, **9**, 341) determined the value of the Weiss magneton number for cobalt salts in aqueous solution and found it to be 25·04. For solutions of $CoCl_2$, $6H_2O$ in methyl, ethyl and amyl alcohols, the Weiss magneton number varied between 22 and 23. In hydrochloric acid solutions, the value lay between 22 and 24. This effect was attributed, therefore, to the formation of $(CoCl_3)'$ and $(CoCl_4)''$ and not due to the production of anhydrous $CoCl_2$ or $CoCl_2$, $2H_2O$, as the Weiss magneton number for these salts as well as for $CoCl_2$ solutions in concentrated sulphuric acid was practically 25.

It is well known that the study of magneto-optic relations throws some light on the nature of ionic "micelle" in solution (*cf.* Bhatnagar and Kapur, *J. Indian Chem. Soc.*, 1934, **11**, 767). It was with this view that the study of magneto-optic rotation of $CoCl_2, 6H_2O$ in different solvents was undertaken.

EXPERIMENTAL.

The method employed for the study of the magneto-optic rotation of the $CoCl_2, 6H_2O$ solutions in different solvents consisted in placing the water-jacketed tube (2·75 cm. long) containing the solution in a solenoid described in a previous paper from this laboratory (*cf.* Mathur and Kapur, *Indian J. Phys.*, 1932, 7, 15) and measuring the rotation produced as a result of magnetic field. A current of 9·5 amp. was passed. The source of light used was a glass mercury vapour lamp with blue filter.

In order to calculate the molecular rotation of a dissolved substance from the measured rotation of the solution, it is assumed that the dissolved substance and the solvent act independently of each other and that the measured rotation is composed additively from the rotation of these two. The assumption leads, therefore, to the following expression for molecular magnetic rotation of solution,

$$d_m = \frac{W \times M_1 \times 100}{W_{H_2O} \times S \times 18 \times a}$$

where w denotes the rotation of the solution, W_{H_2O}, the rotation of water, S, the density of solution, a, the percentage of the substance present in the solution, and M_1, the mol. wt. of the solute.

Then M, the molecular rotation of the solute $= d_m - \mu M_s$ where M_s is the molecular rotation of solvent (for water it is 1) and μ, the number of g. mol. of solvent per mol. of the dissolved substance.

When the solvent is not water, its molecular rotation

$$M_s = \frac{r_1}{r} \times \frac{M}{d \times m}$$

where r_1 denotes the rotation due to solvent; r, the rotation due to water; M, the mol.wt. of the solvent; d, the density of the solvent; and m, the mol.wt. of water.

It is to be expected that if the assumption mentioned above does not hold, the molecular rotation will vary with concentration.

Extra pure Kahlbaum's sample of $CoCl_2$, $6H_2O$ free from nickel was used. The purity of hydrochloric acid, sulphuric acid and amyl alcohol was tested by comparing their molecular magnetic rotations with the values obtained by other workers (*cf.* Table I.)

TABLE I.

Compound.	Molecular magnetic rotation as determined by the authors.	Molecular magnetic rotation as given in literature.
Amyl alcohol	5·91	5·95 (Inter. Crit. Tables)
Sulphuric acid	2·32	2·315 (Perkin, *J. Chem. Soc.*, 1886, **49**, 777)
Hydrochloric acid	3·79	4·00 (Perkin, *ibid.*, 1889, **55**, 680)

The results obtained for the molecular magnetic rotation of cobalt chloride are tabulated below.

TABLE II.

Solvent.		*a.*	*μ.*	*S.*	W/W_{H_2O}.	*M.*
Water		12·52	50·43	1·066	1·133	+ 10·87
		8·36	79·12	1·046	1·088	+ 10·66
		2·544	283·2	1·022	1·057	+ 10·30
Amyl alcohol		3·05	45·81	0·8352	0·987	+ 3·06
		3·442	40·21	0·844	0·943	− 9·14
HCl	30·83%	2·180	50·36 HCl 221·9 H_2O	1·169	1·296	−45·00
	25·58%	2·217	41·05 HCl 235·2 H_2O	1·148	1·276	−28·00
	19·7%	2·277	30·81 HCl 247·4 H_2O	1·117	1·244	−11·2
	13·5%	2·343	20·52 HCl 259·4 H_2O	1·086	1·182	− 1·52

DISCUSSION.

From the results it is clear that the value for molecular magnetic rotation varies with varying concentration. This effect is just noticeable in aqueous solutions, but becomes increasingly prominent in alcoholic and HCl solutions. If the ions in solution remain all of one kind, the molecular magnetic rotation will also remain constant. The fact that the molecular magnetic rotation of cobaltous chloride in alcoholic and HCl solutions varies with concentration, suggests the presence of different ionic carriers. Further, the fact that the colour of the cobaltous chloride solutions in alcohol and HCl also changes with concentration from blue-violet to pink points to the possibility of the magnetic and colour carriers being identical.

On examination of the results we see that the molecular magnetic rotation of cobalt chloride in amyl alcohol solution varies from 3·06 to −9·14 with concentration. In HCl solution the value varies between −1·52 to −45·0, while the value in aqueous solution is 10·58 to 0·3. If the change in colour had only been due to the production of anhydrous cobalt chloride, as suggested by Hartley (*loc. cit.*) and others, the value would have remained constant with change of concentration.

The molecular magnetic rotation for cobalt chloride in concentrated sulphuric acid came to be +1·8. Thus, even if we suppose as suggested by Vaillant (*Compt. rend.*, 1929, **189**, 747; 1930, **190**, 170), that the colour change is brought about both by changing the state of ionisation and by causing dehydration, it is clear from the above experiment that dehydration can be only responsible for bringing the value of molecular magnetic rotation down to +1·8, but the predominant factor is the formation of complex ions of the type $(CoCl_3)'$ and $(CoCl_4)''$ as suggested in a previous publication (*loc. cit.*).

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Received June 8, 1936.

Complex Metal-ammonium Selenites and Selenito-metalammines.

By Priyadaranjan Rây and Amalendra Narayan Ghosh.

Although cobalt complexes containing the sulphito-, sulphato- (Riesenfeld, *Z. anorg. Chem.*, 1924, **132**, 99), chromato- (Briggs, *J. Chem. Soc.*, 1919, **115**, 67) and selenato- (Mayer, *Z. anorg. Chem.*, 1921, **118**, 1) groups have been known for some time, very few attempts have been made to prepare the corresponding selenito-compounds. Only recently Riley (*J. Chem. Soc.*, 1928, 2988) has described the preparation of two pentammine selenito-complexes of cobalt. No other stable complex selenite of cobalt or any other metal has been reported, though Hahn, Seigert and Meir (*Z. anorg. Chem.*, 1926, **150**, 126) have isolated a series of double selenites.

As the important series of sulphito-ammine complexes has been so thoroughly investigated, it seemed desirable to study complexes containing the analogous selenito-group. The preparation and properties of some of these compounds have been described in this paper.

As has been pointed out by Riley (*loc. cit.*), the selenito-radical, like the corresponding sulphito-group, occupies only one co-ordination position inside the complex zone. But contrary to the behaviour of the sulphito-ion, the selenito-ion appears to have very little tendency to enter the complex zone, being readily displaced from the co-ordination sphere by water (hydrolysis). This lack in the power of forming stable complexes may be ascribed to the increased heaviness of the ion and the decreased electronegative character of selenium. Unlike the sulphito-complexes, the selenito-complexes are highly soluble and extremely hygroscopic, their isolation in the solid state in a pure form being rather difficult.

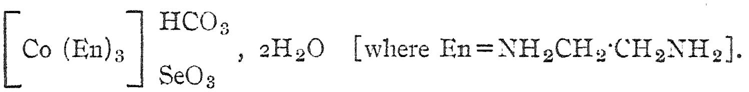
The salts of the series are ruby-red in colour and, by inference from comparison with sulphito-complexes, the selenito-group may be considered to be linked to the central atom through oxygen (*cf.* Werner, *Annalen*, 1911, **386**, 81 ; Duff, *J. Chem. Soc.*, 1922, **121**, 452).

Further, as no ammino- or substituted ammino-complexes of copper and nickel selenites have been reported, the preparation and properties of a few of these complex selenites have been described in this communication.

The nickel selenite gives both tetra- and hexa-co-ordinated ammines, whereas copper-ammine selenites are only tetra-co-ordinated, suggesting an influence of the nature of the anion upon the co-ordination capacity of the central metallic atom.

EXPERIMENTAL.

Triethylenediamine Cobaltic Bicarbonato-selenite



$$\left[\mathrm{Co\,(En)_3}\right]\begin{matrix}\mathrm{HCO_3}\\ \mathrm{SeO_3}\end{matrix},\ 2H_2O \quad [\text{where } En=NH_2CH_2\cdot CH_2NH_2].$$

Cobalt selenite, $CoSeO_3,2H_2O$ (5 g.), prepared by precipitation from a solution of $CoCl_2$, $6H_2O$ by Na_2SeO_3, was shaken with 40 c. c. of a 10% solution of ethylenediamine hydrate. The mixture was oxidised by vigorous current of air for 12 hours. The selenite gradually dissolved and the solution became yellow as the oxidation proceeded. After the oxidation was complete, the filtered solution was concentrated on the water-bath and treated with absolute alcohol. The yellowish brown precipitate was filtered, dissolved in water, and the aqueous solution saturated with CO_2. The solution was again concentrated on the water-bath and again precipitated by alcohol. The yellow crystals were dried to a constant weight in vacuum over H_2SO_4.

The substance forms highly soluble, brownish yellow crystals, which effervesce with dilute acids. Barium chloride gives with the cold and neutral solution a complete precipitation of barium carbonate and barium selenite showing that the HCO_3' and SeO_3'' are outside the complex zone. (Found : N, 18·95 ; Co, 12·64 ; CO_2, 9·85 ; Se, 17·02. Theory requires N, 18·93 ; Co, 12·76 ; CO_2, 9·52; Se, 17·06 per cent).

Triethylenediamine Cobaltic Selenite, $[Co\,(En)_3]_2\,(SeO_3)_3,\ 4H_2O$.

Triethylenediamine cobaltic bicarbonato-selenite, prepared, as described above, was treated with half the molecular proportion of selenious acid dissolved in water. Brisk evolution of CO_2 occurred. The solution was concentrated on the water-bath and the crystals precipitated by absolute alcohol. These were redissolved in water and reprecipitated with alcohol. They were then filtered, washed with absolute alcohol, and dried to a constant weight in vacuum over H_2SO_4. (Found : N, 17·96 ; Co, 12·45 ; Se, 25·50. Theory requires N, 18·04 ; Co, 12·60 ; Se, 25·50 per cent).

The substance forms highly soluble golden yellow crystals. Barium chloride added in excess to a neutral solution causes an immediate and complete precipitation of barium selenite, showing that all the selenium is present as anion.

Diaquo-diethylenediamine Cobaltic Chloroselenite.

$$\left[\mathrm{Co\ En_2\ (H_2O)_2}\right]\begin{matrix}\mathrm{Cl}\\ \\ \mathrm{SeO_3}\end{matrix},\ \tfrac{1}{2}\,\mathrm{H_2O}.$$

Carbonato-diethylenediamine cobaltic chloride, $[\mathrm{Co\ En_2\ (CO_3)}]\ \mathrm{Cl}$ (10 g.) was treated with a solution of selenious acid (5 g.) in the cold, when a rapid evolution of CO_2 occurred. The solution was warmed on the water-bath and was treated, after concentration, with absolute alcohol at 0°. The salt separated as an oil which gradually solidified on repeated washing with alcohol by decantation. The substance was dried in vacuum over H_2SO_4.

It forms highly soluble red-violet hygroscopic crystals. Silver nitrate produces a white precipitate in cold aqueous solution. A part of the precipitate dissolves in nitric acid and the insoluble part in ammonia. This proves that both $\mathrm{Cl'}$ and $\mathrm{SeO_3''}$ are outside the complex zone. (Found : Cl, 9·0, 9·11 ; Co, 15·64, 15·63 ; Se, 20·03, 20·35. Theory requires Cl, 9·16 ; Co, 15·28 ; Se, 20·45 per cent.).

Monaquo-diethylenediamine Selenito-cobaltic Chloride.

$$[\mathrm{Co\ En_2\ (H_2O)\ SeO_3}]\ \mathrm{Cl},\ 2\tfrac{1}{2}\ \mathrm{H_2O}.$$

Cobalt selenite (10 g.), 10% ethylenediamine solution (52 c. c.) and ammonium chloride (2 g.) were mixed and oxidised by a current of air in the cold. The red cobalt selenite gradually dissolved; the air current was continued for some hours after the cobalt selenite had all dissolved. The red solution was concentrated in vacuum over H_2SO_4 and treated with alcohol. Some reddish brown crystals separated; these on analysis, were found to be triethylenediamine cobaltic chloride, $[\mathrm{Co\ En_3}]\mathrm{Cl_3}$, and were filtered off. The mother liquor was again concentrated in vacuum and treated with alcohol. This precipitated an oily liquid which was washed thoroughly with alcohol by decantation and then evaporated to dryness in vacuum over H_2SO_4.

The substance forms highly soluble ruby-red hygroscopic crystals. Cold aqueous solution gives no precipitate with ammoniacal barium chloride solution, but, on boiling, a white precipitate of barium selenite appears. This shows that the selenito-group is present inside the complex. If a very cold solution is treated with an excess of silver nitrate, rapidly filtered and the filtrate boiled, a white precipitate of silver selenite soluble in acid is obtained. But all the selenium is precipitated in the cold if the solution is kept in contact with silver nitrate for any length of time. A gradual hydrolysis of the selenito-complex leading to the formation of a diaquo-compound occurs. (Found : N, 13·78, 13·78; Cl, 8·94, 8·82; Co, 14·51, 14·52; Se, 19·07, 19·35. Theory requires N, 13·79 ; Cl, 8·87 ; Co, 14·52 ; Se, 19·50 per cent).

Cryoscopic measurements.

G. of salt in 100 c.c. soln. calc. on the anhydr. basis.	Depression of F.P. = Δ.	M.W. from $\Delta = m$.	Vant Hoff's factor $i = M/m$.	Degree of dissociation $\alpha = \frac{(i-1)}{(n-1)}$
3·2784	0·340	173·57	2·07	1·07
1·1835	0·130	163·87	2·20	1·20
0·59175	0·070	152·15	2·37	1·37

where *M* denotes the mol. wt. calculated and *n*, the number of ions into which the substance should dissociate.

The value of α indicates that the salt is considerably hydrolysed in aqueous solution. The determination of equivalent conductivity also points to the same conclusion.

Conductivity measurements at 25°

v (litres) ⟶	16	32	64	128	256	512	1024
λ_v for $[CoEn_2(H_2O)SeO_3]Cl$	91·2	103·6	115·6	121·4	139·3	150·6	157·7
$[CoEn_2(SO_3)]Br$	—	89·32	99·24	108·1	115·1	122·8	127·6
$[CoEn_2(S_2O3)]Br$	—	83·18	90·65	96·90	104·1	113·0	118·5
$[CoEn_2(SO_4)]Br$	—	90·4	98·5	106·9	114·0	119·7	125·2

The conductivity values of the last three compounds are those given by Duff (*J. Chem. Soc.*, 1922, **121**, 454).

Aquodiethylenediamine Selenito-cobaltic Nitrate.

$[Co\,En_2(H_2O)\,SeO_3]NO_3{\cdot}2H_2O$.

Cobalt selenite (10 g.), 10% ethylenediamine solution (52 c.c.), and ammonium nitrate (2·5 g.) were mixed and oxidised, when almost all the selenite dissolved; the solution was filtered and further oxidised for two hours. The deep red solution was concentrated on the water-bath and then left in the ice-chest for a few hours. The cooled solution was afterwards treated with alcohol; and the oily liquid, that separated, was washed with alcohol by decantation. This was dried to a constant weight in vacuum over H_2SO_4.

The substance forms red hygroscopic powder resembling the chloride in properties. It is much more easily hydrolysed than the chloride. Silver nitrate completely precipitates all selenium even in the cold. Ammoniacal solution of barium chloride does not precipitate barium selenite in the cold. The precipitate appears only on heating the solution. (Found : N, 17·72 ; Co, 14·07 ; Se, 18·80. Theory requires N, 17·65 ; Co, 13·98 ; Se, 18·75 per cent).

Aquo-diethylenediamine Selenito-cobaltic Bromide.

$[Co\ En_2\ SeO_3\ (H_2O)]\ Br.$

Cobalt selenite (5 g.), 26 c.c. of ethylenediamine solution (10%) and 1·4 g. of ammonium bromide were mixed and oxidised by a vigorous current of air. The selenite gradually dissolved; the solution was filtered, and the filtrate further oxidised for some hours. The solution was then concentrated on the water-bath and cooled. Yellow crystals of $[Co\ En_3]\ Br_3$ separated out and were filtered off. The filtrate was left in the ice-chest for some hours. The cooled solution was treated with small amount of alcohol to free it from any triethylenediamine compound. When the latter salt separated no more, the selenitobromide was precipitated from the solution as an oil by an excess of alcohol, and washed free from impurities.

It forms deep red extremely hygroscopic powder, shows properties resembling those of the chloride, and is more easily hydrolysed. Barium chloride and excess of ammonia brings about a slow precipitation of barium selenite. (Found : N, 13·83 ; Br, 19·70 ; Co, 13·91 ; Se, 19·62. Theory requirs N, 13·86 ; Br, 19·80 ; Co, 14·06 ; Se, 19·60 per cent).

Aquo-diethylenediamine Selenito-cobaltic Sulphate.

$[Co\ En_2(H_2O)\ SeO_3]_2\ SO_4,\ 2H_2O.$

Cobalt selenite (5 g.), 10% ethylenediamine solution (26 c.c.) and 1 g. of ammonium sulphate were mixed and oxidised as in the above described preparation. The concentrated solution was cooled for 3 hours and was freed from any triethylenediamine salt by repeated treatment with small quantities of alcohol. The solution was then treated with excess of alcohol, when an oily liquid separated, which was washed several times by decantation with alcohol. This was dried to a crystalline powder in vacuum over H_2SO_4.

The substance forms red hygroscopic powder, highly soluble in water. Its properties are similar to those of the other salts. Treated with an excess of ammoniacal barium chloride, the aqueous solution gives an immediate precipitation of barium sulphate (insoluble in acids), and the filtrate gives a precipitate of barium selenite (soluble in acids) on boiling. This shows that SeO_3'' is present inside the complex and SO_4'' exists as an anion. (Found : N, 4·70 ; Co, 14·92 ; Se, 20·36 ; SO_4, 12·33. Theory requires, N, 14·38 ; Co, 14·94 ; Se, 20·36 ; SO_4, 12·30 per cent).

Triethylenediamine Nickel Selenite, $[Ni\ En_3]\ SeO_3$.

Nickel selenite, $NiSeO_3, \frac{1}{2}H_2O$ (5 g.) was treated with 47 c.c. of a 10% ethylenediamine hydrate solution and then digested on the water-bath. The selenite dissolved and the solution turned violet-red ; the filtered solution was evaporated on the water-bath with constant stirring. Pale red, extremely deliquescent crystals were thus obtained. These were dried at 100° to a constant weight.

Barium chloride gives a complete precipitation of barium selenite from its aqueous solution. Acids decompose it readily. Nickel is completely precipitated from an ammoniacal solution of the salt by dimethylglyoxime. (Found : N, 23·16; Ni, 16·25; Se, 21·25. Theory requires N, 23·0 ; Ni, 16·05 ; Se, 21·64 per cent).

Diethylenediamine Nickel Selenite, $[Ni\ En_2]\ SeO_3,\ 1\frac{1}{2}\ H_2O$.

Excess of nickel selenite was digested with ethylenediamine solution. After filtering off the undissolved selenite, the blue solution was concentrated in vacuum over lime. A blue hygroscopic crystalline solid was obtained.

The blue powder is highly soluble in water; the solution on warming decomposes with formation of triethylenediamine salt depositing nickel selenite. Digestion with ethylenediamine hydrate leads also to the formation of the triethylenediamine compound. (Found : N, 16·23; Ni, 17·52; Se, 23·85. Theory requires N, 16·60; Ni, 17·58; Se, 24·0 per cent).

Hexammine Nickel Selenite, $[Ni(NH_3)_6]SeO_3$.

Hydrated nickel selenite was suspended in alcohol and treated with a current of dry ammonia. The selenite gradually dissolved, the solution becoming blue and then violet. From the violet solution, pale violet crystals were precipitated by the continuous passage of ammonia. The unstable violet substance was quickly filtered in a cold funnel, dried in the folds of a filter-paper and introduced into a dried and weighed vessel. This was then dried thoroughly by passing a current of dry ammonia for several hours till the weight became constant.

The substance readily decomposes on exposure to air, first turning blue and then green with complete loss of ammonia. The solid can be kept unchanged in an atmosphere of ammonia at a temperature below 52°—its decomposition point. (Found : NH_3, 35·51; Ni, 19·45; Se, 27·50. Theory requires NH_3, 35·49; Ni, 20·12; Se, 27·50 per cent).

Diethylenediamine Copper Selenite, $[Cu\,En_2]SeO_3$.

A solution of copper sulphate (5 g.) was treated with calculated amount of sodium selenite. The precipitated copper selenite was washed and treated with ethylenediamine solution. The blue solution thus obtained, was evaporated to dryness in vacuum over sulphuric acid to a constant weight.

The substance forms blue hygroscopic crystals having a beautiful violet reflex. It readily dissolves in water forming a deep blue solution and remains unchanged by treatment with ethylenediamine hydrate. It is decomposed on heating in air, and also by acids. Barium chloride solution causes an immediate precipitation of barium selenite in the cold. (Found : N, 18·05; Cu, 20·37; Se, 25·04. Theory requires N, 18·02; Cu, 20·43; Se, 25·49 per cent).

Tetrammine Copper Selenite, $[Cu(NH_3)_4]SeO_3$.

Precipitated copper selenite was treated with dry ammonia. On absorption of ammonia the mass became hot and the colour changed to deep blue. The mass was thoroughly dried by continuous passage of ammonia for some hours till the weight became constant.

The substance forms deep blue hygroscopic crystals decomposing on exposure to air. It dissolves in water forming a blue solution, which readily decomposes by losing ammonia. (Found : Cu, 24·45 ; NH_3, 26·28 ; Se, 30·98. Theory requires Cu 24·61 ; NH_3, 26·28 ; Se, 30·60 per cent).

SUMMARY.

1. The preparation and properties of a number of complex metal-ammonium selenites and selenito-metalammines with Co^{+++}, Cu^{++}, and Ni^{++} as the central atoms and containing ammonia and ethylenediamine have been described.

2. Only in the case of some cobaltic complexes the selenito-group has been found to enter the complex zone, while it exists as an anion in all other cases. The co-ordination bond holding the selenito-group is very weak and is easily ruptured by water (hydrolysis). This might be attributed to the increased heaviness of SeO_3'' and the decreased electronegative character of selenium. Like the sulphito-group, the bivalent selenito group occupies only one co-ordination position.

3. Both tetra- and hexa-co-ordinated nickel-ammine selenites have been obtained, whereas copper-ammine selenites are only tetra-co-ordinated. This suggests an influence of the nature of the anion upon the co-ordinating capacity of the central metallic atom.

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Oxidation of Glucose in presence of Insulin, Glutathione and other Substances and the Probable Mechanism of Biological Oxidations.

By C. C. Palit and N. R. Dhar.

For a number of years, we have investigated the catalytic induced and photochemical oxidations of food materials by air or hydrogen peroxide and in several communications we suggested a probable mechanism of oxidations taking place in the animal body or the plant kingdom or in the soil. This paper is a continuation of the same line of investigation.

It has been shown (*J. Indian Chem. Soc.*, 1934, **11**, 661) that the induced oxidation of glucose by air in presence of ferrous hydroxide acting as an inductor, is greatly increased if small amounts of manganous hydroxide is added to the ferrous hydroxide. Thus the oxidation of glucose in presence of ferrous hydroxide (=0·0468 g.) alone is 4·33% and after the addition of manganous hydroxide (=0·00328 g.) to ferrous hydroxide, the oxidation of glucose is increased to 48·26%. Similarly the induced oxidation of glucose in presence of cerous hydroxide (=0·1069 g.) is accelerated by manganous hydroxide. Hence our results show that the joint action of the two inductors is much greater than their additive values.

We have also shown that small amounts of copper stimulate markedly the induced oxidation of glucose and other food materials.

In this communication, the results on the oxidation of glucose in presence of insulin and glutathione acting singly or in mixtures aided by different inorganic catalysts and solid surfaces have been shown. It is well known that both insulin and glutathione are excellent reducing agents taking up oxygen directly. A mechanism of biological oxidations has also been discussed briefly.

EXPERIMENTAL.

The experimental work was carried on in the same way as described in a previous paper (Palit and Dhar, *J. Indian Chem. Soc.*, 1934, **11**, 661). The following results have been obtained :—

TABLE I.

36·5 litres of air passed in 13 hours. 0·05 G. of glutathione and 10 units of insulin taken. Each of the substances taken as inductor = 1 g. Amount of sodium phosphate added = 0·2880 g. 10 C.c. of glucose = 0·2308 g. of CuO (blank).

Substance used as surface and inductor (1·0 g.).	Percentage amount of oxidation of glucose in presence of			
	substance alone.	substance + 0·2880 g. of Na-phosphate.	substance + 0·05 g. of glutathione.	substance + 0·05 g. of glutathione + 0·2880 g. of Na- phosphate.
Titanium dioxide	19·9	22·4	31·3	49·7
Silica	17·5	25·7	32·9	52·2
Cerous hydroxide	100·0	100·0	97·3	84·5
Ferrous hydroxide	39·8	71·06	34·05	63·86
Manganous hydroxide	65·07	96·4	62·4	83·88

TABLE II.

Conditions same as in Table I.

Substance used as surface and inductor (1·0 g.).	Percentage amount of glucose oxidised in presence of			
	substance + 10 units of insulin.	substance + 10 units of insulin + 0·2880 g. of Na-phosphate.	substance + 10 units of insulin + 0·05 g. of glutathione.	substance + 10 units of insulin + 0·05 g. of glutathione + 0·288 g. of Na-phosphate.
Titanium dioxide	22·0	30·0	27·6	50·4
Silica	18·1	56·1	39·16	53·98
Cerous hydroxide	100·0	100·0	96·66	97·7
Ferrous hydroxide	93·76	86·3	81·8	85·26
Manganous hydroxide	70·5	96·79	64·2	84·7

The results in Table I show that glucose is appreciably oxidised by passing air in presence of solid surface like titanium dioxide, silica, etc., but in presence of the hydroxides of cerium, iron and manganese, which not only act as surfaces but as inductors as well, the oxidation is much greater than with titanium dioxide or silica. When sodium phosphate is added along with the surface, the oxidation is appreciably increased. When glutathione is added, the oxidation in presence of titanium dioxide and silica is also increased but with the hydroxides of cerium, iron and manganese, there is a slight decrease in the oxidation of glucose. In presence of both phosphate and glutathione, the oxidation of glucose is still further accelerated in the cases of titanium dioxide and silica, but with the hydroxides of cerium, iron and manganese, the oxidation in presence of glutathione and phosphate is appreciably less than that with phosphate alone.

From the results recorded in Table II, it is seen that in presence of insulin, the oxidation of glucose aided by titanium dioxide, silica, cerous hydroxide, ferrous hydroxide and manganese hydroxide respectively is increased. In this respect the behaviour of insulin and glutathione is practically the same but in presence of phosphate, insulin seems also to accelerate the oxidation but glutathione appreciably retards the oxidation in presence of phosphate. A mixture of glutathione and insulin is appreciably better than either insulin or glutathione alone with titanium dioxide or silica as surface but with the inductors cerous hydroxide, ferrous hydroxide or manganous hydroxide, a mixture of insulin and glutathione appears to be less effective.

Oxidation of glucose in presence of (i) insulin, (ii) glutathione and and (iii) a mixture of insulin and glutathione containing sodium phosphate and metallic chlorides as inductors.

73·0 Litres of air passed in 30 hrs. 10 C.c. of glucose solution $=0{\cdot}2308$ g. of CuO (blank). 20 C.c. of sodium phosphate solution $=0{\cdot}288$ g. of sodium phosphate.

TABLE III.

Na-phosphate taken in 20 c.c. soln.	Glutathione added.	Insulin added.	$FeCl_3$ in 20 c.c. soln. in terms of Fe_2O_3.	$CuCl_2$ added.	$MnCl_2$ added.	Glucose oxidised.
0·2880 g.	Nil	10 units	Nil	Nil	Nil	22·2%
,,	,,	,,	0·01452 g.	,,	,,	31·7
,,	,,	,,	,,	0·01 g.	,,	23·05
,,	,,	,,	,,	Nil	0·01 g.	19·5
,,	,,	,,	,,	0·01	0·01	22·0

	Na-phosphate taken in 20 c.c. soln.	Glutathione added.	Insulin added.	$FeCl_3$ in 20 c c. soln. in terms of Fe_2O_3.	$CuCl_2$ added.	$MnCl_2$ added.	Glucose oxidised.
TABLE IV	0·2880 g.	0·05 g.	Nil	Nil	Nil	Nil	50·3
	,,	,,	,,	0·01452 g.	,,	,,	64·4
	,,	,,	,,	,,	0·01	,,	56·8
	,,	,,	,,	,,	Nil	0·01	55·6
	,,	,,	,,	,,	0·01	0·01	52·5
TABLE V	0·2880 g.	Nil	10 units	Nil	Nil	Nil	21·4
	,,	,,	,,	0·001452 g.	,,	,,	24·7
	,,	,,	,,	,,	0·0001	,,	26·5
	,,	,,	,,	,,	Nil	0·0001	27·1
	,,	,,	,,	,,	0·0001	0·0001	32·2
TABLE VI	0·2880 g.	Nil	10 units	0·0290 g.	Nil	Nil	66·2
	,,	,,	,,	,,	0·0001	,,	80·4
	,,	,,	,,	,,	Nil	0·0001	77·7
	,,	,,	,,	,,	0·0001	0·0001	81·1
	,,	,,	,,	...	...	...	...
TABLE VII	0·2880 g.	0·05	Nil	Nil	Nil	Nil	51·5
	,,	,,	,,	0·001452 g.	,,	,,	57·6
	,,	,,	,,	,,	0·0001	,,	61·7
	,,	,,	,,	,,	Nil	0·0001	62·4
	,,	,,	,,	,,	0·0001	0·0001	67·3
TABLE VIII	0·2880 g.	0·05	Nil	0·0290	Nil	Nil	77·6
	,,	,,	,,	,,	0·0001	,,	82·0
	,,	,,	,,	,,	Nil	0·0001	79·8
	,,	,,	,,	,,	0·0001	0·0001	85·7
	...	...	...	...	...	...	...
TABLE IX	0·2880 g.	0·05	10 units	Nil	Nil	Nil	58·6
	,,	,,	,,	0·01452	,,	,,	68·2
	,,	,,	,,	,,	0·01	,,	48·0
	,,	,,	,,	,,	Nil	0·01	52·5
	,,	,,	,,	,,	0·01	0·01	48·7
	,,	,,	,,	,,	0·0001	0·0001	72·4
TABLE X	0·2880 g.	0·05	10	Nil	Nil	Nil	56·9
	,,	,,	,,	0·001452	,,	,,	60·3
	,,	,,	,,	,,	0·0001	,,	64·8
	,,	,,	,,	,,	Nil	0·0001	65·5
	,,	,,	,,	,,	0·0001	0·0001	70·2

In a previous publication (Dube and Dhar, *J. Phys. Chem.*, 1932, **36**, 444) we have shown that glucose is oxidised in presence of insulin alone and the amount of oxidation increases by the addition of phosphate. The results in Table III show clearly that the amount of oxidation of glucose is appreciably increased when ferric chloride is added to a mixture of phosphate and insulin and that the amount of oxidation of glucose is retarded by the addition of either cupric chloride or manganous chloride or a mixture of cupric and manganous chlorides to the same amount of ferric chloride. Exactly similar results are obtained using glutathione instead of insulin under identical conditions but the amount of oxidation of glucose in presence of glutathione is far greater than that in presence of insulin as will be evident from Table IV.

From the results in Tables V and VI, it is noticed that the amount of oxidation of glucose in a mixture of insulin and phosphate increases with the concentration of ferric chloride. In other words, the greater the amount of ferric chloride, the greater is the amount of oxidation of glucose. Another interesting fact may be observed that with the same amount of ferric chloride, the amount of oxidation of glucose increases by the addition of very minute amount (traces) of either cupric chloride or manganous chloride or a mixture of both. Hence traces of copper or manganese occurring singly or in mixtures of both act as an accelerator in the oxidation of glucose, whereas in presence of larger amount of copper, manganese or a mixture of both, each one acts as a retarder in the oxidation. Exactly similar results are obtained using glutathione instead of insulin as will be evident from Tables VI, VII and IX. In this case also the amount of oxidation of glucose in presence of glutathione is greater than that in presence of insulin.

The results in Tables IX and X show that the amount of oxidation of glucose in presence of a mixture of glutathione and insulin aided by phosphate and metallic salts is slightly greater than that in presence of glutathione alone.

Mechanism of Biological Oxidations.

It seems that the following agencies are important in bringing about the oxidation of food materials not only in animal life but also in plant respiration :—

(*i*) Reducing agents like glutathione, chlorogenic acid, ascorbic acid, Palladin's "respiratory chromogens," Keilin's cytochrome, Warburg's "ovoflavin", "lactoflavin", internal secretions, etc., are known to take up oxygen directly from the air and are likely to induce the oxidation of food materials. The experiments recorded in this paper show that glucose is oxidised by air in presence of glutathione or insulin.

(*ii*) The surface of plant and animal cells, just as surfaces like SiO_2, TiO_2, etc., accelerate the oxidation of glucose by air.

(*iii*) The presence of small quantities of iron and traces of manganese and copper compounds accelerate the oxidation of glucose by air.

(*iv*) Mild alkalis and phosphates.

(*v*) Sunlight.

In previous publications (*cf.* Dhar "New Conceptions in Biochemistry", 1932) it has been shown that the oxidation of food materials by air is accelerated by mild alkalis and phosphate and sunlight.

All these agencies seem to have their relative importance in causing the oxidation of the food materials possible in the plant and animal tissues, although they are not oxidised in the air outside. There is reason to believe that in animal oxidation, the internal secretions play an important rôle. It is well known that nature hardly depends on one agency in carrying on its mechanism and in bringing about the oxidation of glucose and other oxidisable materials, seems to take recourse to the foregoing agencies, which have been shown to accelerate the oxidation of food materials by air.

Several years ago one of us stated that the internal secretions act as inductors in the oxidation of food materials (*cf.* Dhar, "*Chemie der Zelle und Gewebe*", 1926, **13**, 119). It is gratifying to note that this view is being supported by medical men and Physiologists (*cf.* Wright's "Applied Physiology", Oxford University Press).

SUMMARY.

1. Glucose is appreciably oxidised by passing air in presence of solid surfaces like titanium dioxide, silica, cerium hydroxide, ferrous hydroxide, manganous hydroxide. The oxidation in the case of these hydroxides which also act as inductors, is much greater than with titanium dioxide or silica. In presence of sodium phosphate, the oxidation aided by the above substances is appreciably increased.

2. In presence of glutathione, the oxidation with titanium dioxide or silica is also increased, but with the hydroxides, there is a slight decrease in the oxidation.

3. In presence of both phosphate and glutathione, the oxidation of glucose is still further increased, but with the hydroxides, the oxidation is appreciably decreased and is less than that in presence of phosphate alone.

4. In presence of insulin, the oxidation of glucose with titanium dioxide, silica, and the hydroxides increases. In this respect the behaviour of insulin and glutathione is practically the same. In presence of phosphate, insulin accelerates the oxidations but glutathione retards them. A mixture of insulin and glutathione acts better than either insulin or glutathione with titanium dioxide or silica and appears to be less effective with the hydroxides as inductors.

5. The amount of oxidation of glucose is appreciably increased when ferric chloride is added to a mixture of insulin and phosphate or of glutathione and phosphate, the oxidation in the latter being much greater than in the former.

6. The oxidation in a mixture of insulin and phosphate or of glutathione and phosphate increases with the concentration of ferric chloride. Traces of copper or manganese occurring singly or mixtures of both, act as accelerators, but in presence of larger amounts of the same, each one acts as a retarder in the oxidation of glucose in presence of either insulin and phosphate or glutathione and phosphate.

7. In presence of a mixture of insulin and glutathione aided by phosphate and metallic salts, the oxidation is slightly greater than that of glutathione alone.

8. Reducing agents like glutathione, chlorogenic acid, ascorbic acid, internal secretions, etc., act as inductors taking up oxygen directly from air and thus induce the oxidations of food materials.

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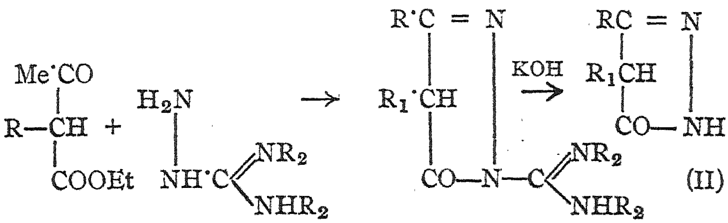
Synthesis in the Pyrazolone Series. Part IV. Action of Aminoguanidines on β-Ketonic Esters and β-Diketones.

By S. C. De and P. C. Rakshit.

In continuation of the work of De, and De and Dutt (*J. Indian Chem. Soc.*, 1926, **3**, 30; 1928, **5**, 459; 1930, **7**, 473) on the synthesis of pyrazolone derivatives by the action of semicarbazide and thiosemicarbazide on β-ketonic esters and β-diketones, the present investigation was undertaken with a view to study if aminoguanidine, which bears a close resemblance in structure to the semicarbazides and which is more basic in nature, behaves in a similar way with β-ketonic bodies. However, it has been found, contrary to expectation that aminoguanidine reacts with ketonic compounds yielding either hydrazones or pyrazolones. The pyrazolones so obtained all contain a carbamidine group, which is quite stable and can be removed only by boiling with an alkali, whereas the carbamide group of the pyrazolones obtained from the semicarbazides are very unstable and can be easily removed.

Acetoacetic ester and its methyl, dimethyl, ethyl and propyl derivatives react with aminoguanidine nitrate slowly in the cold yielding the corresponding pyrazolones, thus :

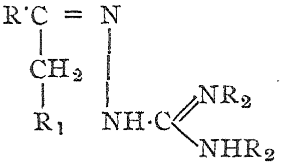


(I) (II)

(R_1=Me, Et, Pr, etc. R=Me; R_2=H)

With the semicarbazides and the thiosemicarbazides, the hydrazones were first formed, which, on treatment with strong ammonia solution yielded pyrazolones (*cf.* De, *loc. cit.*).

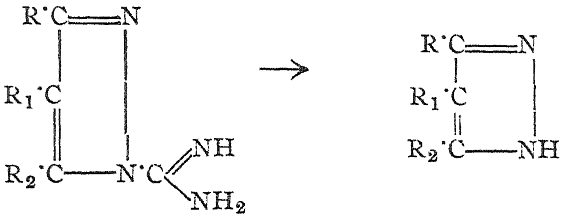
Benzoylacetic ester and aminoguanidine nitrate first gives the hydrazone (III, R=Ph; R_2=H; R_1=CO_2 Et) in the cold; when the alcoholic solution of the hydrazone is heated, the pyrazolone (I, R=Ph; R_1=R_2=H) is produced. Boiling with aqueous caustic potash removes the side-chain forming (II, R=Ph ; R_1=H)



(III)

Both acetoacetic and benzoylacetic esters react with disubstituted aminoguanidine nitrates, first yielding a hydrazone of the type III, (R=Me, Ph; R_2=Ph, C_7H_7, $C_{10}H_7$, etc., R_1=CO_2Et) which changes to pyrazole compounds (I, R=Me, Ph; R_1=H; R_2=Ph, C_7H_7, $C_{10}H_7$ etc.) on heating with glacial acetic acid.

Benzoylacetoacetic ester behaves towards aminoguanidine in the same way as towards semicarbazides, as a diketone and not as a β-ketonic ester to yield the compound (IV, R=Me; R_1=CO_2Et; R_2=Ph). This constitution was determined by boiling it with aqueous caustic potash and acidifying when 3-methyl-5-phenylpyrazole-4-carboxylic acid (V, R=Me; R_1=COOH; R_2=Ph)was obtained.

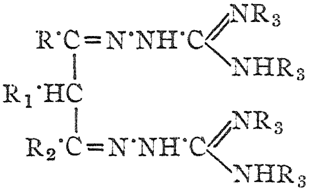


(IV) (V)

With acetosuccinic ester, aminoguanidine yields a pyrazolone derivative (I, R=Me ; R_1=CH_2CO_2Et ; R_2=H), the structure of which is determined by isolating the acid (II, R=Me ; R_1=CH_2CO_2Et) by subsequent hydrolysis with caustic potash and acidifying the product.

In the cold oxalacetic ester yields the pyrazolone derivative (I, R=CO_2Et ; R_1=R_2=H) with aminoguanidine.

Methyl acetylacetone combines with the aminoguanidine producing (VI, $R=R_1=R_2=Me$; $R_3=H$) in the cold, which is converted into a pyrazole (IV, $R=R_2=R_3=Me$), by heating its solution. As before, the carbamidine group can be removed by boiling with caustic potash to obtain trimethylpyrazole (V, $R=R_1=R_2=Me$).

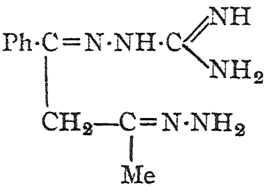


$$\begin{array}{l} R\cdot C{=}N\cdot NH\cdot C\left\langle\begin{array}{l}NR_3\\NHR_3\end{array}\right. \\ \quad\;| \\ R_1\cdot HC \\ \quad\;| \\ R_2\cdot C{=}N\cdot NH\cdot C\left\langle\begin{array}{l}NR_3\\NHR_3\end{array}\right. \end{array}$$

(VI)

In case of ethylacetylacetone, the diaminoguanidine is not obtained, but the pyrazole carbamidine is directly formed in the cold. Benzoylacetone, on the other hand, forms a hydrazone (III, $R=Ph$; $R_2=H$; $R_1=COMe$) in the cold with aminoguanidine. The hydrazone produces the pyrazole compound (IV, $R=Ph$; $R_1=H$; $R_2=Me$). Heated with alkali, the side-chain is removed producing phenylmethylpyrazole (V, $R=Ph$; $R_1=H$; $R_2=Me$) identical with that obtained from benzoylacetone and hydrazine.

The presence of a free CO-group in the hydrazone from aminoguanidine and benzoylacetone (III, $R=Ph$; $R_2=H$; $R_1=COMe$) is proved by the fact that it readily combines with a molecule of hydrazine to yield (VII), which under the conditions of the experiment parts with one molecule of aminoguanidine giving pyrazole (V, $R=Ph$; $R_1=H$; $R_2=Me$). Methylbenzoylacetone behaves in the same way towards aminoguanidine.



$$\begin{array}{l} Ph\cdot C{=}N\cdot NH\cdot C\left\langle\begin{array}{l}NH\\NH_2\end{array}\right. \\ \quad\;| \\ \quad CH_2{-}\underset{\displaystyle Me}{\underset{|}{C}}{=}N\cdot NH_2 \end{array}$$

(VII)

Acetylacetone combines with disubstituted aminoguanidine in hot alcoholic solution to form osazones (VI, $R = R_2 = Me; R_1 = R_3 = H$) of which the compound with di-β-naphthylaminoguanidine undergoes a change to pyrazole with glacial acetic acid, the other osazones remaining unchanged. Benzoylacetone and disubstituted aminoguanidines yield corresponding pyrazoles.

EXPERIMENTAL.

The usual method for the reactions consisted in mixing the concentrated solutions of the reactants in water or alcohol. The mixtures were mostly kept at room temperature, when the insoluble products separated. They were recrystallised several times and then analysed for nitrogen. In a few cases with substituted aminoguanidines the mixtures were heated under reflux. The carbamidine group was removed by boiling with aqueous caustic potash for several hours and then acidifying the solution. The preparation of such a compound is given below in detail, the others are given in a tabular form.

3 - *Methylpyrazolone* - 1 - *carbamidine Nitrate.*—Aminoguanidine nitrate (1·37 g.) was dissolved in the least amount of water to which an alcoholic solution of acetoacetic ester (1·3 g.) was added. It was kept at the room temperature for 2 days, when an appreciable quantity of a solid separated which was filtered off. On allowing the filtrate to evaporate off slowly, a further quantity of the same substance was obtained. Both the crops were twice crystallised from water. It melted at 234° (decomp.). The product is insoluble in ether, chlorofrom, benzene and cold water but appreciably soluble in cold alcohol. (Found : N, 34·8. $C_5H_8ON_4$, HNO_3 requires N, 34·5 per cent).

3-*Methylpyrazolone* was obtained by boiling the above compound with aqueous caustic potash for 3 hours and then neutralising the solution with dilute hydrochloric acid. The solid that separated was crystallised from water and was found to be identical with the compound of Curtius and Jay (*J. pr. Chem.*, 1889, **39**, 52), m. p. 216°.

TABLE I.

Compounds obtained from aminoguanidine nitrate and β-ketonic esters.

β-Ketonic esters.	Product obtained.	Formula.	Crystallised from.	M· p.	Analysis Found.	Analysis Calc.	Remarks.
Me·CO·CH$_2$·COOEt	3-Methylpyrazolone-1-carbamidine nitrate	$C_5H_8ON_4$, HNO_3	Water	234° (d)	N, 34·8%	34·5	
	3-Methylpyrazolone	$C_4H_6ON_2$	Water	216°	—	—	Identified.
Me·CO·CH(Me)·COOEt	3 :4-Dimethylpyrazolone-1-carbamidine nitrate	$C_6H_{10}ON_4$, HNO_3	Water	202° (d)	32·18	32·26	
	3 :4-Dimethylpyrazolone	$C_5H_8ON_2$	Alcohol	262°	—	—	Identified.
Me·CO·CH(Et)·COOEt	3-Methyl-4-ethylpyrazolone-1-carbamidine nitrate	$C_7H_{12}ON_4$, HNO_3	Water	262° (d)	30·45	30·3	Poor yield.
	3-Methyl-4-ethylpyrazolone	$C_6H_{10}ON_2$	Alcohol	228°	22·43	22·2	Compound with the same prepared from N_2H_4 and the ester.
Me·CO·C Me$_2$·COOEt	3 :4 : 4-Trimethylpyrazolone-1-carbamidine nitrate	$C_7H_{12}ON_4$, HNO_3	Water	151° (d)	30·03	30·3	Yield 90%.
	3 :4 :4-Trimethylpyrazolone	$C_6H_{10}ON_2$	Ether	268°	—	—	
Me·CO·CH (Pr)·COOEt	3-Methyl-4-propylpyrazolone-1-carbamidine nitrate	$C_8H_{14}ON_4$, HNO_3	Water	260° (d)	28·87	28·57	
	3-Methyl-4-propylpyrazolone	$C_7H_{12}ON_2$	Alcohol	211°	—	—	Identified with the same obtained from hydrazine and ester.

TABLE I (contd.).

β-Ketonic esters.	Product obtained.	Formula.	Crystallised from.	M.p.	Analysis Found.	Analysis Calc.	Remarks.
Ph·CO·CH$_2$·COOEt	Ethylbenzoylacetate-aminoguanidine nitrate	$C_{12}H_{16}O_2N_4$, HNO_3	Water	200° (d)	N, 22·83	22·5	Yellow crystalline solid formed in cold.
	3-Phenylpyrazolone-1-carbamidine nitrate	$C_{10}H_{10}ON_4$, HNO_3	Water	190°	25·68	26·41	Obtained on heating.
	3·Phenylpyrazolone	$C_9H_8ON_2$	Alcohol	235°	—	—	Identified.
Me·CO·CH (Ph·CO)-COOEt	5-Phenyl-3methyl-4-ethyl carboxylate pyrazole-1-carbamidine nitrate	$C_{14}H_{16}O_2N_4$, HNO_3	Alcohol	222° (d)	20·97	20·89	Pink crystals.
	5-Phenyl-3 methyl-pyrazole carboxylic acid	$C_{11}H_{10}O_2N_2$	Alcohol	262°	13·66	13·86	
Me·CO·CH·COOEt CH$_2$·COOEt	3-Methylpyrazolone-4-ethyl acetate-1-carbamidine nitrate	$C_9H_{14}O_3N_4$, HNO_3	Aclohol	290°	24·03	24·22	Very slow reaction.
	3-Methylpyrazolone-4-acetic acid	$C_6H_8O_3N_2$	Alcohol	240°	—	—	Identified with the compoud from hydrazine and the ester on hydrolysis.
CH$_2$·COOEt CO·COOEt.	3-Ethyl carboxylate pyrazolone-1-carbamidine nitrate	$C_7H_{10}O_3N_4$, HNO_3	Alcohol	224°	26·97	26·82	Poor yield.

TABLE II.

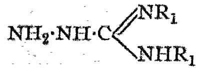
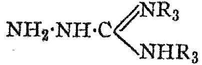
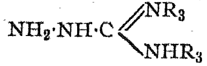
Compounds from aminoguanidine nitrate and β-diketones.

β-Diketone.	Product obtained.	Formula.	Crystallised from	M.p.	Analysis Found.	Analysis Calc.	Remarks.
Me·CO·CH (Me)·CO·Me	Methyl acetylacetone-diaminoguanidine nitrate	$C_8H_{20}O_6N_{10}$	Water	180° (d)	N, 39·68%	39·8	Obtained in cold.
	3 : 4 : 5-Trimethylpyrazole-1-carbamidine	$C_7H_{12}N_4$, HNO_3	Water	202°	32·8	32·6	Obtained on heating above.
	3 : 4 : 5-Trimethylpyrazole	$C_6H_{10}N_2$	Alcohol	138°	—	—	Identified.
Me CO·CH (Et)·CO·Me	3 : 5-Dimethyl-pyrazole-1-carbamidine nitrate	$C_8H_{14}N_4$, HNO_3	Alcohol	174°	30·5	30·6	
	3 :5-Dimethyl-4-ethyl-pyrazole	$C_7H_{12}N_2$	Alcohol	154°	—	—	White needles, identified with the compound from N_2H_4 and the ketone.
Ph·CO·CH₂·CO·Me	Benzoylacetone-amino guanidine nitrate	$C_{11}H_{14}ON_4$, HNO_3	Water	164°	24·63	24·9	Formed in cold.
	3 : 5-Phenylmethylpyrazole-1-carbamidine nitrate	$C_{11}H_{12}N_4$, HNO_3	Water	185°	26·72	26·60	On heating.
	3 :5-Phenylmethylpyrazole	$C_{10}H_{10}N_2$	Water	128°	—	—	Identified with the compound from hydrazine and the diketone.
Ph·CO·CH (Me)·CO·Me	Methylbenzoyl-acetone-aminoguanidine nitrate	$C_{12}H_{16}ON_4$, HNO_3	Water	151°	23·6	23·7	Poor yield.
	3-Phenyl-4 : 5 dimethyl-pyrazole-1-carbamidine nitrate	$C_{12}H_{14}N_4$, HNO_3	Alcohol	192°	25·43	25·27	On heating.

TABLE III.

Compounds from β-diketones and disubstituted aminoguanidines.

They were all crystallised several times from dilute alcohol for purification.

Disubstituted aminoguanidine.	β-Diketone.	Product obtained.	Formula.	M.p.	Analysis Found.	Analysis Calc.	Remarks.
 $NH_2\cdot NH\cdot C\left\langle\begin{matrix}NR_1\\ NHR_1\end{matrix}\right.$	$Me\cdot CO\cdot CH_2\cdot CO\ Me$	Acetylacetone-di-(di-β-naphthylaminoguanidine)	$C_{47}H_{40}N_8$	210°	N, 15·77%	15·64	On refluxing in alcohol.
		3 :4-Dimethyl-pyrazole-1-di-β-naphthylcarbamidine	$C_{26}H_{22}N_4$	185°	14·56	14·35	On heating the above compound in glacial acetic acid.
$NH_2\cdot NH\cdot C\left\langle\begin{matrix}NR_2\\ NHR_2\end{matrix}\right.$	,,	Acetylacetone-di-(di-p-tolyl-aminoguanidine)	$C_{35}H_{40}N_8$	210°	19·80	19·58	
 $NH_2\cdot NH\cdot C\left\langle\begin{matrix}NR_3\\ NHR_3\end{matrix}\right.$	,,	Acetylacetone-di-(di-phenyl aminoguanidine)	$C_{31}H_{32}N_8$	225°	21·93	21·70	On refluxing in alcohol.
 $NH_2\cdot NH\cdot C\left\langle\begin{matrix}NR_3\\ NHR_3\end{matrix}\right.$	$Ph\cdot CO\cdot CH_2\cdot CO\ Me$	Benzoylacetone-di-(di-phenyl aminoguanidine)	$C_{36}H_{34}N_8$	115°	19·51	19·37	
		3-Phenyl-5-methylpyrazole-1-diphenylcarbamidine	$C_{23}H_{20}N_4$	230°	15·76	15·90	Heating the osazone in glacial acetic acid.
$NH_2\cdot NH\ C\left\langle\begin{matrix}NR_2\\ NHR_2\end{matrix}\right.$	,,	Benzoylacetone-di-(di-p-tolyl aminoguanidine)	$C_{40}H_{42}N_8$	146°	17·5	17·66	
		3-Phenyl-4 methylpyrazole-1-di-p-tolylcarbamidine	$C_{25}H_{24}N_4$	220°	15·01	14·73	

=β-Naphthyl R_2=p-Tolyl R_3=Phenyl.

TABLE IV.

Compounds from the disubstituted aminoguanidines and β-ketonic esters.

All the products were purified by crystallisation from dilute alcohol.

$R_1 = \beta$-Naphthyl; $R_2 = p$-Tolyl; $R_3 =$ Phenyl.

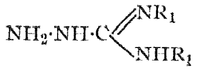
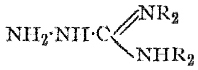
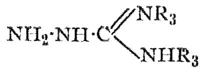
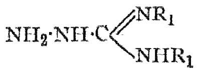
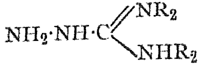
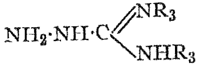
β-Ketonic ester.	Disubstituted aminoguanidine.	Product obtained.	Formula.	M.p.	Analysis Found.	Analysis Calc.
$Me\cdot CO\cdot CH_2\cdot COOEt$	 $NH_2\cdot NH\cdot C\begin{cases} NR_1 \\ NHR_1 \end{cases}$	Ethyl acetoacetate-di-β-naphthylaminoguanidine	$C_{27}H_{26}O_2N_4$	141°	N, 12·64	12·78
		3-Methylpyrazolone-1-di-β-naphthylcarbamidine	$C_{25}H_{20}ON_4$	290°	14·19	14·28
,,	 $NH_2\cdot NH\cdot C\begin{cases} NR_2 \\ NHR_2 \end{cases}$	Ethyl acetoacetate-di-p-tolyl aminoguanidine	$C_{21}H_{26}O_2N_4$	258°	15·48	15·30
		3-Methylpyrazolone-1-di-p-tolylcarbamidine	$C_{19}H_{20}ON_4$	210°	17·66	17·5
,,	 $NH_2\cdot NH\cdot C\begin{cases} NR_3 \\ NHR_3 \end{cases}$	Ethylacetoacetate-diphenylaminoguanidine	$C_{19}H_{22}O_2N_4$	242°	16·83	16·57
		3-Methylpyrazolone-1-diphenylcarbamidine	$C_{17}H_{16}ON_4$	198°	19·37	19·17
$Ph\cdot CO\cdot CH_2CO_2Et$	 $NH_2\cdot NH\cdot C\begin{cases} NR_1 \\ NHR_1 \end{cases}$	Ethylbenzoylacetate-di-β-naphthylaminoguanidine.	$C_{32}H_{28}O_2N_4$	219°	11·0	11·2
		3-Phenylpyrazolone-1-di-β-naphthylcarbamidine	$C_{30}H_{22}ON_4$	180°	12·54	12·33

TABLE IV (contd.).

β-Ketonic ester	Disubstituted amino-guanidine.	Product obtained.	Formula.	M. p.	Analysis Found.	Analysis Calc.
Ph·CO·CH$_2$COOEt	 $NH_2{\cdot}NH{\cdot}C(=NR_2)NHR_2$	Ethylbenzoylacetate-di-*p*-tolyl-aminoguanidine.	$C_{26}H_{28}O_2N_4$	225°	N, 12·94%	13·08
		3-Phenylpyrazolone-1-di-*p*-tolyl-carbamidine.	$C_{24}H_{22}ON_4$	249°	14·80	14·66
„	 $NH_2{\cdot}NH{\cdot}C(=NR_3)NHR_3$	Ethyl-benzoyl acetate-diphenyl aminoguanidine	$C_{24}H_{24}O_2N_4$	232°	14·27	14·00
		3-Phenyl-pyrazolone-1-diphenyl carbamidine	$C_{22}H_{18}ON_4$	206°	15·95	15·81

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An *X*-Ray Investigation of the Crystals of *p*-Nitrodiphenyl.

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The crystallographic examination of the crystals of *p*-nitrodiphenyl shows that they develop *m* {110}, *c* {001}, *x* {121}, *a* {100}, *b* {010} faces, the *m* and the *c* faces being the most predominant ones. If crystallised from a mixture of acetone and amyl acetate they develop, in addition to the above faces, (0kl) or (hkl) and also (189) and sometimes though rarely (111) faces.

The crystals belong to the orthorhombic bipyramidal class and the axial ratios are $a : b : c = 1{\cdot}0218 : 1 : 0{\cdot}6629$ (*cf.* Groth, "Chemische Krystallographie", V, p. 12).

The substance was prepared by standard laboratory methods and crystals were obtained by very slow evaporation from a mixture of acetic acid and acetone. The interfacial angles were measured on the 'Universal photogoniometer' (*cf. J. Sci. Inst.*, 1929, **6**, 11, 343) by suitably mounting a small crystal on the crystal holder with the desired zone axis coincident with the axis of rotation. The angles measured in this way are given below :—

I. Faces parallel to the length of the crystal.

Face No. 1 : Face No. 2 = 88°40′
" " 2 : " " 3 = 91°18′
" " 3 : " " 4 = 88°45′
" " 4 : " " 1 = 91°19′

II. The angle between the end-faces and any one of the above faces was found to be 90°.

These measurements show that the crystal under examination has two sets of parallel faces which are *m* {110} and *m′* {1̄10} faces, the end-faces being the *c* {001} faces. This was further confirmed by taking two Laue photographs from the *m* and *m′* faces ; these were identical showing thereby the correctness of the identification of the faces of the crystal.

The rotation photographs about *a*, *b*, and *c* axes were taken using a very fine beam of *X*-rays from a Shearer gas tube fitted with a copper anticathode. A crystal weighing a fraction of a mg. only was employed. The lengths of the axes were calculated from the spots on the rotation photographs (*vide* Plates I, II and III) and were found to be

$$a = 23{\cdot}25\,\text{Å}, \qquad b = 11{\cdot}38\,\text{Å}, \qquad c = 7{\cdot}55\,\text{Å}.$$

The axial ratios are $a : b : c = 2{\cdot}043 : 1 : 0{\cdot}6633$.

Rotation photographs.

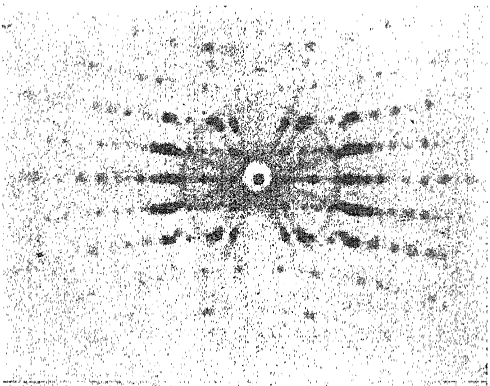

PLATE I.

About b-axis
$D = 4{\cdot}04$ cm.

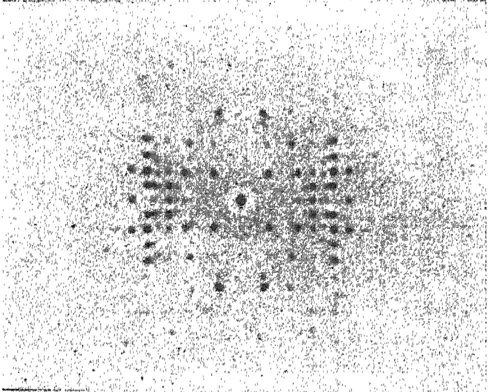

PLATE II.

About a-axis
$D = 4{\cdot}04$ cm.

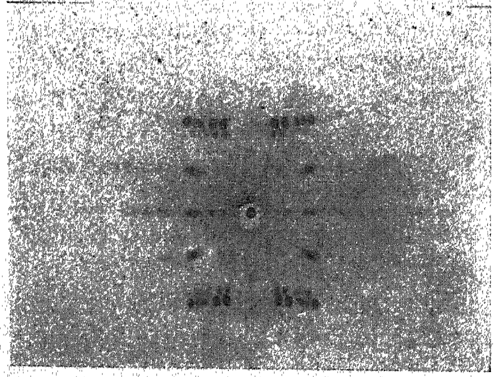

PLATE III.

About c-axis
$D = 4{\cdot}04$ cm.

The *a*-axis is, therefore, twice of that given in Groth (*loc. cit.*).

Oscillation photographs were taken about the *a*, *b*, and *c* axes at intervals of 15° and spots appearing on these were indexed by Bernal's method of analysis (*Proc. Roy. Soc.*, 1926, **A 113**, 117). The planes observed are given in Tables I and II. The comparative values of their intensities marked against each plane were determined by eye estimation as suggested by Robertson (*Proc. Roy. Soc.*, 1928, **A 118**, 712).

TABLE I.

Axial planes.	Prism planes (okl).	Prism planes (hol).	Prism planes (hko).	
002 m. s	021 v. s	102 v. s	210 v. s	620 w
004 v. w	022 s	104 v. w	220 v. s	630 w
200 v. s	023 w	204 w	230 w. m	640 w
400 s	041 w. m	302 m. s	240 w. m	810 w
600 m. s	042 v. w	304 w. m	250 w	840 w. m
800 w. m	043 w. m	402 s	260 w	850 w
1000 w	061 v. w	404 w. m	410 w. m	1010 w. m
1200 v. w	...	502 w. m	430 w. m	1030 w
020 v. s	...	504 w. m	440 w. m	1210 w
...	...	702 v. w	450 v. w	1220 w
...	...	802 w. m	460 v. w	...
...	...	902 w. m	610 m. s	...
...	...	1002 v. w	...	...

TABLE II.

General planes.

111 m. s	311 m	523 w	811 v. w
112 v. s	312 m. s	532 w	812 w
113 v. w	313 w	533 v. w	813 w
121 v. s	314 w. m	541 w	821 m
122 s	321 w	542 v. w	822 w. m
123 v. w	322 s	543 v. w	823 v. w
131 v. w	323 w. m	551 w	831 v. w

TABLE II (contd.).

General planes.

134	w	324	v. w	611	w	841	w. m
141	w	331	v. w	612	w	842	w
142	w. m	333	w. m	614	w	851	w
143	w	341	w. m	621	v. w	911	w
151	v. w	343	v. w	622	w	921	v. w
161	v. w	351	v. w	623	w	922	v. w
211	w	361	w	631	w. m	931	w. m
212	v. s	411	m. s	632	w	941	w
213	w	412	m. s	633	v. w	1011	v. w
214	w	413	v. w	641	w	1012	v. w
221	m. s	414	w. m	642	v. w	1021	v. w
222	m. s	421	w. m	651	w	1022	v. w
223	v. w	422	w. m	711	v. w	1031	w
224	m	431	v. w	712	w.	1032	w
231	w	433	w	713	w	1041	v. w
233	w	441	w	721	m	1111	v. w
241	v. w	443	w	722	v. w	1112	w
242	w. m	451	v. w	723	w	1121	w
243	v. w	461	w. m	731	w. m	1131	w
251	w. m	512	w	732	v. w	1211	v. w
252	v. w	513	v. w	741	w	1221	w
261	v. w	514	w	742	v. w	...	
...		521	w	751	w	...	
...		523	w	752	w	...	

Table I shows that (okl) planes are halved when k is odd, (hol) planes are halved when l is odd and (hko) planes are halved when h is odd. The crystal, therefore, belongs to the space group Q_h^{15} with Γ_o Bravais lattice (Astbury and Yardley, *Phil. Trans.*, 1924, **A**, **224**, 221).

The number of molecules in the unit cell required by this space group is eight. The number of molecules in the unit cell, calculated from the dimensions of the unit cell and the specific gravity of the crystals (1·328) is also eight (8·02 accurately). This shows that the molecules in the unit cell are asymmetric.

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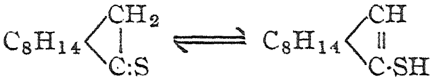
Studies in the Camphor Series. Part III. Tautomeric Behaviour of Thiocamphor and the Activity of its Sodium Derivative.

By Dines Chandra Sen.

The formation of *iso*nitrosothiocamphor (Sen, *J. Indian Chem. Soc.*, 1935, **12**, 647) shows that the methylene group adjacent to C:S in thiocamphor is reactive. The isolation of *C*-substituted benzylidene derivatives of thiocamphor as well as *S*-substituted alkyl derivatives shows that thiocamphor forms two sodium derivatives corresponding to its two tautomeric forms (I) and (II) (*cf.* Tautomerism in camphor, Bredt-Savelsberg, Heinemann, Catherinus and Eibel, *J. pr. Chem.*, 1924, *ii*, **107**, 65 ; 1927, **115**, 235).



$$C_8H_{14}\left\langle\begin{matrix}CH_2\\|\\C{:}S\end{matrix}\right. \rightleftharpoons C_8H_{14}\left\langle\begin{matrix}CH\\\|\\C\cdot SH\end{matrix}\right.$$

(I) (II)

The electronegative influence of C : S-group is apparently greater than that of C : O-group as expected from dipole mements (C : O= 2·5; C:S=3. *cf.* Sidgwick 'The Covalent Link in Chemistry', *p.* 153). This is substantiated by the greater tendency of thioketones to form *S*-substituted alkyl derivatives.

The condensation of sodio thiocamphor with benzaldehyde, anisaldehyde, *o*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde gives *C*-benzylidene derivatives, since they yield the oximes of the benzylidene derivatives of camphor. As the corresponding *dl*-camphor derivatives and their oximes are mostly unknown, they have also been prepared by the usual method (*cf.* Haller, *Compt. rend.*, 1891, **113**, 24; 1895, **121**, 36; 1909, **148**, 1490; Wootton, *J. Chem. Soc.*, 1910, **97**, 410). It has been observed that a small quantity of thioborneol is always formed when metallic sodium is used in these reactions instead of sodamide. A similar phenomenon has also been observed in the case of camphor which gives small quantity of borneol when sodium is used for the preparation of sodio camphor (Brühl, *Ber.*, 1891, **24**, 3373). This is most probably due to the reduction of thiocamphor as well as camphor by means of nascent hydrogen which is evolved during its replacement by means of sodium.

These benzylidene derivatives of thiocamphor, unlike those of camphor, are highly coloured crystalline substances. Of these benzylidene and *p*-methoxybenzylidene-thiocamphor are violet, the nitrobenzylidene derivative is blue, and *p*-dimethylaminobenzylidene derivative is dark red. These products show in a beautiful manner the influence of substituents in the benzene ring on the chromophoric effect of C:S-group in thiocamphor.

The action of alkyl iodides on the sodio derivative of thiocamphor exclusively gives *S*-substituted derivatives. The products are pale green in colour and have got a faint smell resembling that of organic sulphides, but on keeping, the products slowly decompose developing a strong mercaptanic smell. They readily decolourise dilute solutions of bromine and acid permanganate in the cold. When hydrolysed by means of dilute sulphuric acid (10%), they give corresponding mercaptans and camphor, the alkyl mercaptans being identified through their lead salts, and corresponding disulphides obtained by their oxidation with iodine. When treated with organic bases like aniline, nitroaniline or phenylhydrazine, they give alkyl mercaptans.

EXPERIMENTAL.

Benzylidene-thiocamphor.—Thiocamphor (10 g.) in sodium-dried benzene (100 c.c.) was treated with finely powdered sodamide (2·5 g.) and the mixture was boiled on the water-bath for nearly 1 hour. Benzaldehyde (6·5 g.) was added to the mixture, cooled in ice. After keeping overnight the product was poured into crushed ice, the benzene solution washed with water, dried over anhydrous sodium sulphate and allowed to evaporate. Purple crystals associated with a viscous liquid separated out, the oil was removed on a porous tile and the residue crystallised from petroleum ether (b.p. 30°-50°) (charcoal). It was obtained as violet plates, m.p. 105°, yield 5 g. It is soluble in common organic solvents giving a violet solution with green fluorescence. (Found: C, 78·89: H, 8·1 ; S, 12·37. $C_{17}H_{20}S$ requires C, 79·7 ; H, 7·8 ; S, 12·5 per cent).

The *Oxime*, prepared with hydroxylamine hydrochloride and sodium acetate, crystallised from alcohol as colourless, hexagonal plates, m.p. 200°. (Found: N, 5·32. $C_{17}H_{21}ON$ requires N, 5·5 per cent).

Benzylidene-dl-*camphor Oxime* was prepared by heating for 4 hours at 100°, hydroxylamine hydrochloride and benzylidene-*dl*-camphor (m.p. 82·5°), prepared from *dl*-camphor. Haller records m.p. 78°. It crystallised from alcohol as colourless hexagonal plates, m.p. 200°, yield 1·5 g. (Found: N, 5·41. $C_{17}H_{21}ON$ requires N, 5·5 per cent).

p-*Methoxybenzylidene*-dl-*thiocamphor*, prepared from thiocamphor (10 g.), sodamide (2·4 g.) and anisaldehyde (8·5 g.), crystallised from petroleum ether as purple prismatic needles, m.p. 118°, yield 5·5 g. It is soluble in ether, benzene, alcohol, chloroform etc., giving brown solutions with green fluorescence. [Found : C, 75·55 ; H, 8·01; OMe, 10·3 ; M. W. (cryoscopic in benzene) 290. $C_{18}H_{22}OS$ requires C, 75·53; H, 7·7 ; OMe, 10·84 per cent. M. W, 286]. The *oxime* melts at 171°. (Found : N, 5·03. $C_{18}H_{23}O_2N$ requires N, 4·91 per cent).

p-*Methoxybenzylidene*-dl-*camphor* was prepared from camphor (10 g.), sodamide (2·5 g) and anisaldehyde (9 g.) and it was crystallised from petroleum ether as colourless prismatic needles, m.p. 101°, yield 5 g. (Found : C, 80·2 ; H, 8·25. $C_{18}H_{22}O_2$ requires C, 80·0 ; H, 8·15 per cent). The *oxime* was prepared by the action of hydroxylamine hydrochloride (2 g.) on *p*-methoxybenzylidenecamphor (2 g.) in pyridine (10 c.c.), m.p. 171°, yield 1·2 g. (Found : N, 5·02. $C_{18}H_{23}O_2N$ requires N, 4·91 per cent).

p-*Dimethylaminobenzylidene*-dl-*thiocamphor* was obtained from thiocamphor (10 g.), molecular sodium (1·5 g.) and *p*-dimethylaminobenzaldehyde (9 g.) in benzene (100 c.c.). It crystallised from alcohol or petroleum ether as silky red, prismatic needles, m.p. 91°, yield 3·5 g. (Found: C, 75·86 ; H, 8·65 ; N, 4·78; S, 10·65. $C_{19}H_{25}NS$ requires C, 76·25; H, 8·36 ; N, 4·68 ; S, 10·7 per cent).

o-*Nitrobenzylidene*-dl-*thiocamphor* crystallises from petroleum ether as prismatic needles, m.p. 135°. (Found : C, 67·3 ; H, 6·65; N, 4·85; S, 10·71. $C_{17}H_{19}O_2NS$ requires C, 67·77 ; H, 6·31 ; N, 4·65 ; S, 10·63 per cent). The substance has a deep blue colour in the solid state and gives a bluish violet solution. The *oxime* crystallises from alcohol as prismatic needles, m.p. 199°. (Found : N, 9·55. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent).

S-*Methylthiocamphor* or *Methylbornylene Sulphide*.—Thiocamphor (10 g.) was converted to the sodium derivative by the action of sodamide (2·5 g.); and methyl iodide (10 g.) was added to the mixture at 0° and left for 12 hours after which it was heated under reflux on the water-bath for 2 hours. The mixture was cooled and treated with ice-cold water. The benzene solution was washed with water, dried over anhydrous sodium sulphate, benzene evaporated and the liquid distilled at 85-88°/12 mm., yield 3 g. (Found: C, 72·3; H, 9·7; S, 17·43. $C_{11}H_{18}S$ requires C, 72·52; H, 9·9; S, 17·58 per cent). The colourless liquid has got the smell characteristic of sulphides but on keeping it slowly decomposes and develops mercaptanic smell.

Hydrolysis of S-Methylthiocamphor.—*S*-methylthiocamphor (2 g.) and sulphuric acid (10%, 20 c.c.) were heated on a sand-bath at 150-60°. The evolved mercaptan was led through a delivery tube attached to the condenser into lead acetate solution when it formed yellow lead salt crystallisable from alcohol which shrinks at 143° and melts at 165° (decomp.). The mercaptan has also been identified as dimethyl disulphide formed by passing the product into an alcoholic solution of iodine. The solution is diluted with water, extracted with ether, dried over sodium sulphate and distilled at 110°. (Found: S, 68·65. Calc. for $C_2H_6S_2$: S, 68·1 per cent). A solid distilled with water vapour into the condenser, which was scraped out and crystallised from alcohol and identified to be camphor, m.p. 178° (mixed m.p.).

S-*Ethylcamphor*, prepared by the same method as described in the case of *S*-methylcamphor, has b.p. 105°/8 mm. (Found: C, 73·31; H, 10·42; S, 16·48; M. W., 198. $C_{12}H_{20}S$ requires C, 73·47; H, 10·2; S, 16·33 per cent.; M.W., 196). It has got a faint smell resembling that of sulphides, but on keeping for a few days it gives the smell of mercaptans. It decolourises cold, dilute solutions of bromine and acid permanganate. On hydrolysis with 10% sulphuric acid as described above, it gives ethylmercaptan characterised by its lead salt, m.p. 150°, and camphor, m.p. 178°. On heating with aniline or phenylhydrazine it gives ethylmercaptan which was identified by oxidising it to diethyl disulphide, b.p. 153°. (Found: S, 52·52. Calc. for $C_4H_{10}S_2$: S, 52·46 per cent).

My sincere thanks are due to Sir P. C. Rây for his kind interest in this investigation and for the facilities given in his laboratory. My thanks are also due to Mr. S. K. Saha and Mr. N. C. Guha, for some of the analytical results by micro and semi-micro methods.

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The Quaternary Ammonium Iodides of Dimethyl-*p*-toluidine.

By M. Q. Doja.

Thomsen (*Ber.*, 1877, **10**, 1586) first obtained the methyl iodide of dimethyl-*p*-toluidine by the repeated treatment of *p*-toluidine with methyl iodide (*cf.* Hübner, Toile and Athenstadt, *Annalen*, 1884, **224**, 337; Wedekind, *Ber.*, 1902, **35**, 773; Von Braun, *Ber.*, 1908, **41**, 2137). Any other alkiodide of dimethy-*p*-toluidine has not been described so far. The effect of the systematic addition of alkyl iodides to dimethyl-*p*-toluidine has now been studied and it has been found that the alkyl iodides of dimethyl-*p*-toluidine possess a great tendency towards the formation of syrups (*cf.* Jones, *J. Chem. Soc.*, 1903, **83**, 1406; Ullmann, *Annalen*, 1903, **327**, 111), as found earlier in the case of dimethylaniline by Wedekind (*Annalen*, 1901, **318**, 90; *cf.* Menschutkin, *Z. physikal. Chem.*, 1890, **6**, 41; Winkler and Hinshelwood, *J. Chem. Soc.*, 1935, 1147).

The yield of the quaternary iodides of dimethyl-*p*-toluidine together with the corresponding values for dimethylaniline are given below.

Alkyl iodide.	Yield with dimethylaniline.	Yield with dimethyl-*p*-toluidine.
Methyl iodide	88·9%	93·8%
Ethyl iodide	16·2	27·7
Propyl iodide	28·1	40·0
Butyl iodide	17·0	32·0
Amyl iodide	38·7	42·0

It will be seen that there is an alternate decrease and increase with rise in the series. There is a sharp drop in the yield from the methyl iodide to the ethyl iodide, then the differences become less pronounced as we ascend the homologous series. It will also be noted that the yield of the quaternary ammonium iodide of dimethyl-*p*-toluidine is in every case greater than the corresponding compound of dimethylaniline, an observation quite in conformity with the modern conception of electronics.

EXPERIMENTAL.

The reactants in each of the experiments described below were mixed together in a 50 c.c. flask provided with a condenser and a calcium chloride guard tube.

The quaternary iodides are all soluble in water, methyl alcohol, ethyl alcohol and chloroform but insoluble in ether, benzene, toluene, xylene and hexane. In the last liquid they turn yellow in the cold and brown on boiling. Unless otherwise stated the quaternary iodides were all recrystallised from absolute alcohol with a little animal charcoal forming colourless crystals.

The melting points recorded were all determined in Mason's electrical melting point apparatus in sealed tubes and the action of heat was also studied in a test tube (0·3″ × 3·0″) in a glycerine bath.

Trimethyl-p-*tolylammonium Iodide.*—Methyl iodide (2·0 g.) and dimethyl-*p*-toluidine (1·75 g.) were each dissolved in 10 c. c. of ether, well mixed, allowed to stand for 24 hours and then heated on the water-bath for 9 hours. After cooling the separated solid was filtered at the pump and washed with ether, yield 3·52 g.

From dilute solutions in absolute alcohol the substance slowly crystallises in colourless transparent bipyramids (*cf.* Wedekind, *Ber.*, 1899, **32**, 517). It is not hygroscopic in the pure state (*cf.* Vorländer and Siebert, *Ber.*, 1919, **52**, 304). A mixture with ether turns gradually yellow when exposed to air and diffused light (*cf.* Datta and Ghosh, *J. Amer. Chem. Soc.*, 1914, **36**, 1021.) It sublimes unchanged at 206-210° and melts at 202°. (Found: N, 5·21, 5·17, 5·11; I, 45·83, 45·76; $C_{10}H_{16}NI$ requires N, 5·05; I, 45·85 per cent).

Dimethyl-p-*tolylethylammonium Iodide.*—Dimethyl-*p*-toluidine (3 g.) and ethyl iodide (3·5 g.) were each dissolved in 20 c.c. of benzene, mixed together and heated for 18 hours on a water-bath. On cooling a solid separated which was filtered, washed with benzene (5 c.c.), and quickly placed in a vacuum desiccator. After continuous evacuation for 8 hours the solid was left in the desiccator for 4 days. The dry solid was dissolved in cold absolute alcohol and ether added until a precipitate was just obtained. The mixture was placed in a frigidaire and the addition of ether continued twice a day until no further precipitation took place. The separated solid was filtered, washed with a mixture of ether and alcohol (10:1), and dried (1·8 g). It was recrystallised from absolute methyl alcohol (charcoal) as transparent bipyramids, m. p. 196°. It dissolves with difficulty in cold acetone but easily on boiling. It is soluble with great difficulty in carbon disulphide even on boiling. It turns brownish on the surface at 107-110° and sublimes with partial decomposition at 208-11°. (Found: N, 5·02, 4·95, 4·88; I, 43·28, 43·36, 43·29. $C_{11}H_{18}NI$ requires N, 4·81; I, 43·64 per cent).

Dimethyl-p-*tolyl*-n-*propylammonium Iodide.*—Dimethyl-*p*-toluidine (2 g.) and *n*-propyl iodide (2·5 g) were heated on the steam-bath for 22 hours. On keeping for 2 weeks crystals embedded in a thick reddish brown syrup were obtained. The mass was dissolved in absolute alcohol and ether added to the solution placed in the frigidaire till no further precipitation occurred. The supernatent liquid was poured off and the solid pressed on a porous plate and dried, m. p. 200°, yield 1·8 g. When heated in a test tube it begins to melt at 197° and the liquid sublimes with slight decomposition at 199°. (Found: N, 4·56, 4·66, 4·71; I, 41·29, 41·25, 41·37. $C_{12}H_{20}NI$ requires N, 4·59; I, 41·64 per cent).

Dimethyl-p-*tolyl*-n-*butylammonium Iodide.*—Dimethyl-*p*-toluidine (1·5 g.) and *n*-butyl iodide (2 g.) were heated for 16 hours on a steam-bath. On keeping for a fortnight, the slightly syrupy crystalline mass was dissolved in absolute alcohol and ether slowly added until a precipitate was just formed. It was then placed in the frigidaire and 10 c.c. of ether gradually added every day until no more precipitation took place. The precipitated solid was filtered off, washed with ether and dried (1·12 g.). The compound is obtained as a compact mass of transparent laminæ, m.p. 201-2°. It is insoluble in ligroin but rapidly turns brownish yellow in the cold and reddish brown on heating. When heated in a test tube it sublimes unchanged at 198-205°. (Found: N, 4·43, 4·58, 4·50; I, 39·86, 39·73, 39·77. $C_{13}H_{22}NI$ requires N, 4·38; I, 39·81 per cent).

Dimethyl-p-*tolyl*-n-*amylammonium Iodide.*—Dimethyl-*p*-toluidine (2 g.) and *n*-amyl iodide (3 g.) were mixed together and left for 24 hours. The solution was then gently heated in a Babo's bath for 25 minutes. and the white solid thus produced allowed to stand for a couple of days. The compound was dissolved in warm absolute alcohol, the solution cooled and ether added until no further precipitation took place. The solid was filtered, washed with a mixture of ether and alcohol (20:1) and dried (2·10 g). It was recrystallised from benzene-alcohol (1:1) with a little animal charcoal as microscopic crystals, m. p. 199-201°. When heated in a test tube it turns brownish on the surface in some places at 106°, which colour disappears at 162° and then sublimes with slight decomposition at 192-97°. (Found: N, 4·31, 4·53, 4·42 ; I, 37·88, 38·43, 38·37. $C_{14}H_{24}NI$ requires N, 4·20 ; I, 38·14 per cent).

*Dimethyl-*p*-tolylallylammonium Iodide.* — Dimethyl-*p*-toluidine (2 g.) and allyl iodide (2·5 g.) were mixed together, when after a few minutes a vigorous reaction ensued and the reaction mixture began to boil. The mixture was cooled and then allowed to stand for 24 hours. It was then heated on a boiling water-bath for 5 hours. After keeping for 3 weeks the thick syrup was dissolved in absolute alcohol (35 c.c.), placed in the frigidaire and treated with ether (40 c.c.) and 300 c.c. of ether was dropped into the solution placed in the frigidaire and the solution left for 4 days in the frigidaire. Rosettes of crystals mixed with a thick reddish brown syrup separated out. The ether was poured off and the crystals dried on a porous plate, when yellowish flattened needles (0·93 g.) were obtained, m. p. 197°. When heated in a test tube it turns yellowish at 102°-108° and sublimes with slight decomposition at 193-98°. (Found: N, 4·69, 4·67, 4·86; I, 42·11; 41·78, 41·83. $C_{12}H_{18}NI$ requires N, 4·62 ; I, 41·91 per cent).

*Dimethyl-phenyl-*n*-amylammonium Iodide.*—Dimethylaniline (3 g.) and *n*-amyl iodide (5 g.) were mixed together and after 1 hour the mixture was gently heated on a sand-bath for 15 minutes. The solid produced after a vigorous reaction was left for 24 hours, dissolved in cold absolute alcohol (180 c.c.) and then treated with ether (270 c.c.). The mixture was allowed to stand for 10 minutes, the separated solid filtered, washed with 10 c.c. of ether and dried (3·1 g). It is obtained as glistening mica-like thin flakes, m.p. 205°. It dissolves with difficulty in hot acetone giving a light yellow solution. It does not dissolve in ligroin but turns yellow first and then brown. When heated in a test tube it sublimes gradually unchanged at 204-218°. (Found: N, 4·42, 4.44, 4·57; I, 39·78, 39·83. $C_{13}H_{22}NI$ requires N, 4·38; I, 39·81 per cent).

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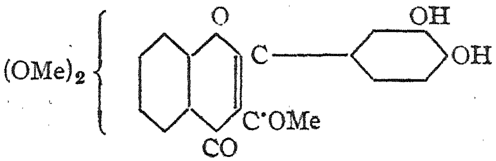
Chemical Examination of *Cuscuta Reflexa*, Roxb. Part IV. Isolation of a New Yellow Flavone Colouring Matter from the Seeds.

By Radha Raman Agarwal.

In previous communications from these laboratories the chemical examination of the stems of *Cuscuta reflexa*, Roxb (Syn. Amarbel) has been fully described by Agarwal and Dutt (*J. Indian Chem. Soc.*, 1935, **12**, 384, 586). In the present investigation the seeds of this drug have been put to a thorough examination.

Dymock ("Pharmacographica Indica", Vol II, p. 548) separated a bitter and glucosidal resin from the seeds in addition to quercitrin. An alkaloidal principle was also present in traces which failed to give any special colour reactions. As a result of our investigations we have been able to isolate a fixed oil (3%), cuscutalin (0·05%), a flavone colouring matter called by the author as amarbelin (0·1%), amorphous bitter resin (1·0%) and reducing sugars. The oil has already been worked up separately (Agarwal and Dutt, *J. Indian Chem. Soc.*, 1936, **13**, 264). Amarbelin has the molecular formula $C_{18}H_{16}O_7,H_2O$ and preliminary examination readily reveals its nature as a colouring matter belonging to the flavone group. It gives a deep green colour with ferric chloride and forms a diacetyl and dibenzoyl derivative. The determination of the methoxyl groups in the usual manner establishes the presence of three methoxyl groups in the molecule. This proves that it is a dihydroxytrimethoxyflavone. Caustic potash fusion of amarbelin gives protocatechuic acid and a phenol which could not be identified due to lack of sufficient material but it does not give tests for phloroglucinol. Amarbelin is stable to atmospheric oxidation in alkaline solution which points to a methoxyl group being in position 3. The remaining two methoxyl groups seem to be present in the fused benzene ring. The following constitution is suggested at present for amarbelin.



Demethylation of amarbelin in the usual manner gives a product which could not be obtained in a state of sufficient purity for analysis, but its alkaline solution is not stable to aerial oxidation proving thereby the presence of a flavonol derivative. It is not identical either to quercitin or morin, and has been named amarbelitin.

Pharmacologically amarbelin is supposed to give interesting results in view of the fact that calycopterin, isolated by Ratnagiriswaran and others (*Biochem. J.*, 1934, **28**, 1964) from the leaves of *Calycopteris floribunda,* which was shown to be a dihydroxytetramethoxyflavone was found to have anthelmintic properties. Since the seeds are also reputed to be anthelmintic a thorough and detailed study of its physiological properties will be undertaken at the King George's Medical College, Lucknow.

EXPERIMENTAL.

An authentic sample of the seeds of *Cuscuta reflexa* was obtained from the Punjab, dried in shade and was crushed to a fine powder. When burnt completely it left 10·28% of a dirty white ash consisting of 25·05% of water-soluble and 74·95% of water-insoluble inorganic material. The following radicals and elements were detected in the ash: sodium (traces), potassium, calcium, magnesium, carbonates, phosphates, chlorides and nitrates.

Sample of finely crushed material was then extracted in a Soxhlet's apparatus successively when the following amounts of extracts dried at 100° were obtained.

Benzene extract (3%).—A green coloured oil was obtained.

Chloroform extract (4%).—A yellowish green coloured mass giving colour with ferric chloride and a yellow precipitate with lead acetate was obtained. It reduces Fehling's solution.

Ethyl acetate extract (5·9%).—A yellow amorphous mass, which gives a deep green colour with ferric chloride and a deep yellow precipitate with alcoholic lead acetate. It reduces Fehling's solution and ammoniacal silver nitrate. With alkalis a beautiful yellow colour is developed.

Acetone extract (2·8%).—A yellow amorphous mass having properties similar to above.

Alcoholic extract (9·6%).—A greyish yellow amorphous mass. The powdered material (3·5 kg.) was repeatedly extracted with benzene and the dark green coloured oil obtained (105 g.) was worked up separately (*cf.* Agarwal and Dutt, *loc. cit.*) The defatted mass of the seeds was then dried completely from benzene and extracted several times with ethyl alcohol (96%). The combined alcoholic extracts were then concentrated till the major portion of the solvent was removed, whereby a greenish orange yellow syrupy mass was obtained (300 g.) It was then thoroughly refluxed with benzene in order to remove oil and chlorophyll and dissolved in alcohol. The alcoholic solution was treated with an excess of alcoholic lead acetate to remove tannins. The lead salt was decomposed in the usual manner but nothing crystalline or chemically definite product could be isolated.

The tannin-free original alcoholic extract was then evaporated to dryness and the residue dissolved in hot water. The aqueous solution was next treated with a solution of basic lead acetate and the yellow precipitate obtained was collected, washed thoroughly with water and decomposed by sulphuretted hydrogen in alcoholic suspension. The yellow alcoholic solution after removal of lead sulphide was then freed from hydrogen sulphide by passing a current of air, and evaporated to dryness under reduced pressure. The reddish yellow brittle amorphous mass was washed repeatedly with ether and carbon disulphide and crystallised several times from hot water as soft lemon yellow tufts, m. p. 234°, yield 3·45 g. It crystallises from dilute alcohol in clusters of needles.

It has been named *amarbelin* after the Indian name of the plant from which it has been obtained. It is easily soluble in ethyl and methyl alcohols, acetone, ethyl acetate, glacial acetic acid, pyridine, less so in chloroform, benzene, nitrobenzene, amyl alcohol and water and insoluble in carbon disulphide, petroleum ether, ligroin, toluene and ether. It dissolves in sodium carbonate solution and in caustic alkalis with a bright yellow colour and is reprecipitated on acidification. The alkaline solution is sufficiently stable to aerial oxidation. It dissolves in concentrated sulphuric acid (bright yellow colour which changes to orange yellow on warming), concentrated nitric acid (red) and in concentrated hydrochloric acid (pale yellow). With alcoholic ferric chloride it gives a green colour and with alcoholic lead acetate a deep yellow precipitate, and a chocolate silver salt with silver nitrate. The yellow solution of the substance in glacial acetic acid is turned crimson red on the addition of a drop of concentrated sulphuric acid and greenish black which gradually turns brownish on the addition of ferric chloride. It forms crystalline oxonium salts with mineral acids and with alcoholic potassium acetate yellow needles are slowly deposited on keeping. It gives no derivatives with hydroxylamine, phenylhydrazine or semicarbazide, does not reduce Fehling's solution and is non-glucosidic in character. In methyl alcoholic solution the substance on treatment with metallic magnesium and hydrochloric acid gives a bright red solution showing that it is a colouring matter belonging to the flavone group. [Found (in sample dried at 120°)] : C, 62·8, 62·4; H, 5·0, 4·8. $C_{18}H_{16}O_7$ requires C, 62·79; H, 4·65 per cent. Found (air dried sample): C, 59·2, 59·75; H, 5·5, 5·45; H_2O, 4·3 ; M.W. (lead salt) 359, 352 (ebulliscopic in alcohol) 348, 352; OMe, 26·1, 25·1, 25·9. $C_{15}H_7O_4$ $(OMe)_3$, H_2O requires C, 59·7; H, 5·0; H_2O, 4·9; OMe, 25·6 per cent. M.W., 362].

The *Lead salt* was formed as bright yellow amorphous mass. (Found: Pb, 22·8. $C_{36}H_{30}O_{14}$ Pb requires Pb, 23·2 per cent).

The *Silver salt*, prepared from the ammonium salt and silver nitrate in the usual manner, was obtained as a chocolate powder. (Found: Ag, 23·2. $C_{18}H_{15}O_7Ag$ requires Ag, 22·9 per cent).

Diacetylamarbelin, obtained by heating for 2 hours amarbelin (0·8 g.), acetic anhydride (5 c.c.) and a few drops of pyridine, crystallised from alcohol in colourless small needles, m.p. 152°. It gives no colouration with alkaline solutions. (Found: C, 61·49; H, 5·0. $C_{22}H_{20}O_9$ requires C, 61·69; H, 4·67 per cent).

Dibenzoylamarbelin, prepared from amarbelin (1 g.), pyridine (25 c.c.) and benzoyl chloride (10 c.c.) in the usual manner, solidified on keeping for about a week. It crystallised from alcohol in microscopic colourless needles, m.p. 160° (decomp.) after previous shrinking at 124°. It gives no colour with caustic soda. (Found: C, 69·22; H 4·50. $C_{32}H_{24}O_9$ requires C, 69·56; H 4·35 per cent).

Amarbelitin.—Amarbelin (0·8 g.) was heated with hydroiodic acid (*d* 1·79, 12 c.c.) in an oil-bath at 130-135° for about 5 hours. After leaving overnight the reddish yellow flakes of amarbelitin hydroiodide were decomposed by boiling with acetic acid and water for about half an hour. It crystallised from aclohol (charcoal) as colourless flakes, shrinking at 190° and melting at 204-205° (decomp.). It is very slightly soluble in water and readily soluble in alcohol. An alcoholic solution gives an olive green colour with ferric chloride which becomes brownish red on keeping. It gives a reddish orange precipitate with alcoholic lead acetate. It gives a beautiful yellow colour with sodium hydroxide. A sufficient quantity of amarbelitin was not obtained for analysis.

Caustic potash fusion of Amarbelin.—Amarbelin (2 g.) and caustic potash (20 g. in 5 c.c. of water) were heated together for 4 hours at 120-130° in a nickel crucible till the yellow colour was changed to brown. The melt on cooling was extracted with water and neutralised with sulphuric acid. A dirty brown amorphous product separated which was filtered, washed and crystallised from dilute alcohol as cream coloured micro-crystalline powder, m.p. 168°. The quantity obtained was too small to admit of identification.

The filtrate was then repeatedly extracted with ether, the ethereal solution extracted with saturated solution of sodium bicarbonate. The bicarbonate extract was neutralised with sulphuric acid and concentrated, whereby a chocolate coloured substance separated. The mother liquor was extracted with ether and ethereal extracts evaporated to dryness. The combined product was then purified through its lead salt when colourless needles were obtained, m.p. 194°. It is soluble in alcohol, acetone, ethyl acetate and less so in water. It gives a reddish colouration with ferric chloride and reduces ammoniacal silver nitrate. From all its reactions and properties it is identified as protocatechuic acid. A mixed m.p. with Merck's pure protocatechuic acid is 194°.

The phenolic portion, obtained after the separation of the acid by bicarbonate, extraction of the ether and evaporation of the solvent, was dissolved in caustic soda. On working it up in the usual manner an amorphous substance was obtained from which nothing definite could be isolated. It failed to give any reaction for phloroglucinol.

The resin of the decomposed basic lead salt obtained after the separation of amarbelin by water failed to give any other product. It was of a dark greyish brown colour with a metallic lustre and melted indefinitely at 100-104°, yield 35 g.

The filtrate after the separation of the lead salt by basic lead acetate was freed from lead by passing a current of sulphuretted hydrogen and concentrated. It reduced Fehling's solution readily and contained a large amount of reducing sugars.

In conclusion the author wishes to express his deep sense of gratitude to Dr. S. Dutt, D.Sc. for his valuable help and guidance. He

is also indebted to the 'Kanta Prasad Trust' of the Allahabad University for grant of a research scholarship which enabled him to investigate this problem.

SUMMARY.

1. A flavone colouring matter named amarbelin has been isolated from the seeds of *Cuscuta reflexa*, Roxb.

2. Amarbelin has been shown to be a dihydroxytrimethoxyflavone. Amarbelin gives protocatechuic acid on caustic potash fusion. Demethylation of amarbelin gives a product different from quercitin or morin and named as amarbelitin.

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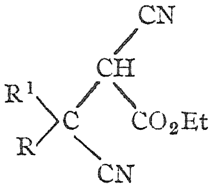
Spiro-compounds. Part I. A New Route to Spiro-compounds. Synthesis of *cyclo*Hexane-spiro-*cyclo*pentane

BY NRIPENDRA NATH CHATTERJEE.

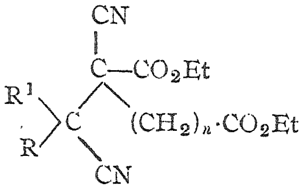
The valency deflexion hypothesis has been supported by Thorpe, Ingold and co-workers by the work on the formation and stability of spiro-compounds (*cf.* Thorpe and co-workers, *J. Chem. Soc.*, 1915, **107**, 1080; 1919, **115**, 320; 1921, **119**, 1199; 1922, **121**, 1496; 1926, 2011; Kon, *ibid.*, 1921, **119**, 810; 1922, 573; Birch, Gough and Kon, *ibid.*, 1921, **119**, 1315; Paul, *J. Indian Chem. Soc.*, 1931, **8**, 717).

The methods available for the preparation of such compounds are limited in number and a new general method has been described in this paper. This consists in condensing the sodium salt of the dicyano ester (I), formed by the condensation of a ketone-cyanohydrin with ethyl sodiocyanoacetate (Higson and Thorpe, *J. Chem. Soc.*, 1906, **89**, 1455) with a monohalogenated ester to yield the product (II).

This on hydrolysis gives an acid, the triethyl ester (III) of which, when subjected to the Dieckmann condensation yields the product (IV).



(I)



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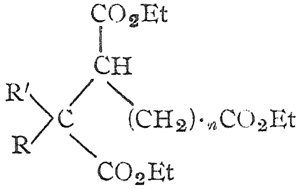

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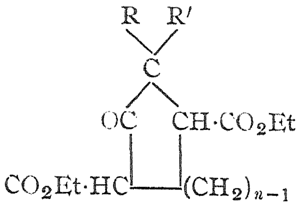
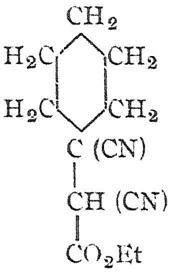


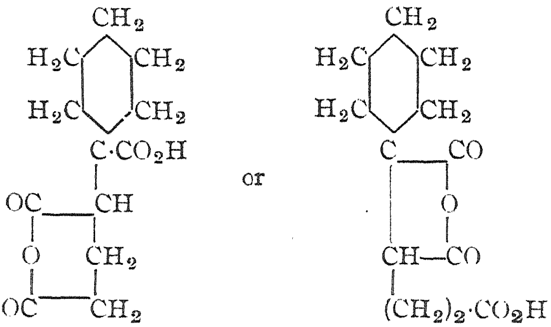
(IV)

(R, R′ are either alkyl groups or parts of different ring systems and *n* may have numerical values ranging from 1 to 3).

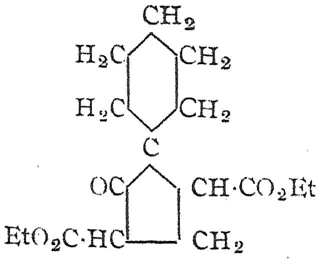
For the synthesis of *cyclo*hexane-spiro-*cyclo*pentane the following method has been adopted. Freshly distilled *cyclo*hexanone cyanohydrin is allowed to react with the sodium salt of ethyl cyanoacetate (*cf.* Dickens, Horton and Thorpe, *J. Chem. Soc.*, 1924, **125**, 1830), when the sodium derivative of ethyl 1-cyano*cyclo*hexane-1-cyanoacetate (V) is obtained. It is then allowed to react with ethyl β-chloropropionate when diethyl 1-cyano*cyclo*hexane-1-α-cyanoglutarate is obtained in good yield. When hydrolysed by means of sulphuric acid (70%) the latter yields an anhydride (VI) (corresponding ester is obtained on esterification). The acid anhydride yields 1-carboxy*cyclo*hexane-1-α-glutaric acid on treatment with caustic alkali. Triethyl *cyclo*hexnae-1-carboxylate-1-α-glutarate, obtained by esterifying the above acid, gives diethyl *cyclo*hexane-spiro-*cyclo*pentane-2-one-3:5-dicarboxylate (VII), when heated in benzene solution in presense of sodium. This ester gives a violet colouration in alcoholic solution with ferric chloride and it has got a peculiar fruity smell characteristic of the series. This ester on hydrolysis gives *cyclo*hexane-spiro-*cyclo*pentane-2-one-5-carboxylic acid (VIII). It shows all the properties of a keto-acid and on oxidation yields *cyclo*hexane-1 : 1-dicarboxylic acid. By the Clemmensen reduction of the keto-acid (VIII), *cyclo*hexane-spiro-*cyclo*pentane-5-carboxylic acid is obtained, which gives *cyclo*hexane-spiro-*cyclo*pentane (IX) on decarboxylation by heating the calcium salt with lime. This hydrocarbon has previously been obtained by the reduction of 2-keto*cyclo*hexane-spiro-*cyclo*pentane (*Ber.*, 1929, **62**, 2180. *cf.* also *J. Chem Soc.*, 1933, 353) which in turn is obtained either by treating the reduction product of *cyclo*pentanone with sulphuric acid (Maiser, *Ber.*, 1899, **32**,2055,) or by the action of sulphuric acid on $\triangle^{9:10}$-octahydronaphthalene oxide (Hückel, *Annalen*, 1929, **474**, 121) or by the action of zinc and ethyl bromoacetate on $\triangle^{9:10}$-octalin oxide (Clemo and Ormston, *J. Chem. Soc.*, 1932, 1780).



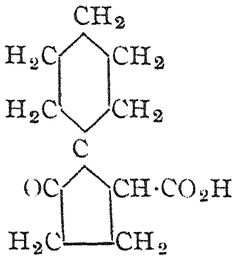
(V)



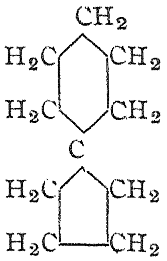
(VI)



(VII)



(VIII)



(IX)

The crude product obtained by the Clemmensen reduction of *cyclo*hexane-spiro-*cyclo*pentane-2-one-5-carboxylic acid when heated with selenium yields naphthalene. Such a type of ring transformation (*cf.* Clemo and Ormston, *J. Chem. Soc*, 1933, 352), may be explained by supposing that the system migrates to a stable form at high temperature, the spiro-compound is first transformed into decalin and then dehydrogenation takes place with the formation of naphthalene.

EXPERIMENTAL.

*Diethyl-*1*-cyano*cyclo*hexane-*1*-α-cyanoglutarate.*—To a well-cooled solution of freshly distilled *cyclo*hexanone cyanohydrin (186 g.) in absolute alcohol (186 c. c.), a suspension of ethyl sodiocyanoacetate, obtained from ethyl cynoacetate (168 g.), sodium (33 g.) and alcohol (500 c. c.), was gradually added with vigorous shaking. The mixture after being kept in ice for 6 hours and at room temperature for 3 days, was mixed with ethyl β-chloropropionate (230 g.) and after the initial reaction had abated was boiled under reflux until it was neutral to litmus (about 40 hours). The mixture was filtered and the filtrate diluted with water and extracted with ether, the ethereal solution washed with water, dried and the ether removed. The ester distilled as a viscous liquid, b. p. 220°-25°/8 mm., yield 160 g. (Found: C, 63·4; H, 7·3. $C_{17}H_{24}O_4N_2$ requires C, 63·7; H, 7·5 per cent).

1*-Carboxy*cyclo*hexane-*1*-α-glutaric Acid.*—The foregoing ester (20 c. c.) could not be hydrolysed with concentrated hydrochloric acid even on prolonged boiling. It was mixed with sulphuric acid (70 %, 120 c. c.) and boiled under reflux for 12 hours. The condenser was removed from the flask from time to time to allow the alcohol formed to escape. The solution was then diluted with water and extracted with ether, and the ethereal solution was treated with sodium carbonate. On acidification of the carbonate solution the compound (VI) was obtained which was heated on a water-bath with a solution of caustic alkali (15%) for 3-4 hours. The alkali solution was then acidified and extracted with ether. After removing ether the product was kept in a desiccator when it solidified. It crystallised from dilute hydrochloric acid, m. p. 165° (decomp.), yield *12* g. (Found: C, 56·2; H, 6·8. $C_{12}H_{8}O_{6}$ requires C, 55·8; H, 6·9 per cent).

The crude acid anhydride (II) was esterified by passing alcohol vapour through a mixture of it in alcohol containing sulphuric acid. The product obtained after working up in the usual manner was found to distill in vacuum, but solidified on attaining the laboratory temperature. It was crystallised from ether, m. p. 46°. (Found: C, 62·5; H, 7·4. $C_{14}H_{20}O_5$ requires C, 62·6; H, 7·4 per cent).

Triethyl cyclo*hexane-*1*-carboxylate-*1*-α-glutarate* was obtained in an almost quantitative yield from the acid by the alcohol vapour method. In a typical experiment the acid (25 g.), absolute alcohol (75 c. c.) concentrated sulphuric acid (7 c. c.), 3 litres of vapourised alcohol (3-4 hours) gave 26 g. of the ester, b. p. 164°/4 mm. (Found : C, 63·7 ; H, 8·6. $C_{18}H_{30}O_6$ requires C, 63·1 ; H, 8·8 per cent).

Diethyl cyclo*hexane-spiro-*cyclo*pentane-*2*-one-*3:5*-dicarboxylate*, (VII).—A mixture of the foregoing ester (10 g.) and granulated sodium (1·2 g.) in dry benzene (25 c. c.) was refluxed for 10 minutes to start the reaction The heating was discontinued until the vigour of the reaction abated and was then continued for 2 hours. After cooling, the product was treated with cold dilute sulphuric acid and the benzene layer was washed with aqueous sodium carbonate and with water, dried and evaporated. The residue in alcoholic solution gave a violet colouration with ferric chloride. The ester was obtained as a pale yellow oil (5 g.), b. p. 174°/4 mm. (Found : C, 64·6 ; H, 8·0. $C_{16}H_{24}O_5$ requires C, 64·8 ; H, 8·1 per cent).

cyclo*Hexane-spiro*cyclo*pentane-*2*-one-*5*-carboxylic Acid*, (VIII).—The ester (VII) was refluxed with excess of dilute sulphuric acid (20%) for 12 hours and the cooled solution saturated with ammonium sulphate and repeatedly extracted with ether, and the extract washed with water and dried. After removing the ether it was kept in a desiccator when it crystallised as needles, m. p. 102° (after previous softening). (Found : C, 67·5 ; H, 8·1. $C_{11}H_{16}O_3$ requires C, 67·4 ; H, 8·1 per cent).

Ethyl cyclo*hexane-spiro-*cyclo*pentane-*2*-one-*5*-carboxylate*, prepared by refluxing a solution of the keto-acid (10 g.) in absolute alcohol (40 c. c) with the addition of absolute alcohol (5 c. c.) saturated at 0° with hydrogen chloride, formed a colourless viscous oil (7 g.), b. p. 132°/5 mm. (Found : C, 70·9 ; H, 8·2. $C_{13}H_{20}O_3$ requires C, 69·6 ; H, 8·9 per cent). The *Semicarbazone* crystallised from absolute alcohol, m. p. 201°. (Found : N, 14·6. $C_{14}H_{23}O_3N_3$ requires N, 14·9 per cent).

cyclo*Hexane-spiro-*cyclo*pentane*.—The pure keto-acid (5 g.) amalgamated zinc (30 g.) and concentrated hydrochloric acid (45 c. c.) were refluxed for 12 hours, further acid (30 c. c.) was then added and the heating continued for 12 hours. By extraction with ether a product was obtained which even on keeping for a long time in a vacuum desiccator over sulphuric acid did not solidify. This product showed no properties of a ketone but when the calcium salt was heated with lime in vacuum *cyclo*hexane-spiro-*cyclo*pentane was obtained as an oil in a very poor yield. It was fractionated several times and the fraction at 63°-75°/15 mm. was collected and was converted into a bromo derivative, m. p. 130-32°. (Found : Br, 70·3. Calc. for $C_{10}H_{14}Br_4$: Br, 70·4 per cent).

Dehydrogenation of cyclo*Hexane-spiro-*cyclo*pentane-5-carboxylic Acid.*—The crude acid (5 g.) and selenium (25 g.) were heated at 280°-290° for 20 hours. The temperature was then raised to 330° and maintained for 30 hours. The reaction product was extracted several times with light petroleum (b. p. 40°-60°). After removing the petroleum the residue was distilled over sodium in vacuum, when after fractionation, a small quantity of naphthalene was obtained, m. p. 80° alone or mixed with an authentic specimen of naphthalene The picrate melted at 148°-49° (mixed m. p.)

Oxidation of cyclo*Hexane-spiro-*cyclo*pentane-2-one 5-carboxylic Acid.*—The keto-acid (3 g.) was warmed with an excess of concentrated nitric acid untill most of the red fumes disappeared. The resulting solution was then boiled for a few minutes and finally evaporated to dryness. The residue was treated with water and again evaporated ; the semi-solid mass, thus obtained, was left on a porous plate and after crystallising from water the cyclohexane-1:1-dicarboxylic acid melted at 176° (decomp.) (lit. m. p. 176°). On heating it loses carbon dioxide, giving an acid, m. p. 31°, which proved to be identical with hexahydrobenzoic acid.

My sincere thanks are due to Professor Dr. P. C. Mitter for encouragement and advice during the course of this work.

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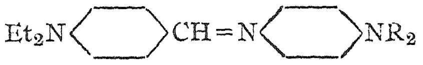
Preparaiion of *p*-Diethylaminobenzaldehyde.

By M. Q. Doja and A. Mokeet.

An attempt has been made to prepare *p*-diethylaminobenzaldehyde in quantity. The patent of Böhringer (D. R. P. 108026) as recorded in Winther's Patente der Organischen Chemie was followed with modifications. In spite of many variations with regard to relative proportion of reactants and other details, nothing crystalline could be isolated. Methods for the preparation of alloxantin and alloxan from uric acid (*cf.* Biltz and Max, *Ber.*, 1921, **54**, 2451) and diethylanil-alloxan (*cf.* Fettizari, *Gazzetta* , 1887, **17**, 412) are recorded in the experimental sequel.

Ullmann and Frey (*Ber.*, 1904, **37**, 860 ; *cf. ibid.*, 1905, **38**, 524) obtained *p*-diethylaminobenzylidene-*p*-aminodimethylaniline (I, R=Me) by the interaction of diethylaniline, formaldehyde and nitrosodiethylaniline. We made an extensive study of this reaction



(I)

but could not isolate the aldehyde after the hydrolysis of (I, R=Me).

The substance (I, R=Et) was also prepared but it also did not give the aldehyde on hydrolysis. Further work is in progress.

EXPERIMENTAL.

In the crystallisation of all the compounds described below, a little animal charcoal was used together with the solvent.

Uric acid (20 g.) and dilute hydrochloric acid (78 c. c.) were heated on a water-bath at 35-37°, and finely powdered potassium chlorate slowly sprayed into the mechanically stirred mixture until a clear solution was obtained. The cold solution was diluted with water (152 c. c.), allowed to stand (50 minutes) and then filtered. Through the filtrate a brisk current of sulphuretted hydrogen was passed for about 20 minutes, the solution left aside (22 hours), cooled in a frigidaire (2 hours) and filtered. The solid was washed with cold water, dissolvod in hot water and filtered. The filtrate was evapoated to dryness (yellowish crystals, 15 g.). After two recrystallisations from hot water, colourless rhombic prisms were obtained, m. p. 201-202°* (decomp.). (Found: C, 30·1 ; H, 3·0 ; N, 17·2. $C_8H_{10}O_{10}N_4$ requires C, 29·8 ; H, 3·1 ; N, 17·4 per cent).

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* The melting points recorded were all determined in sealed tubes.

Alloxan.—Alloxantin (9 g.) was treated with a mixture of concentrated (12 g.) and fuming (18·5 g.) nitric acids and the mixture left in a fume cupboord for 5 days. The solid obtained was dried, yield 8·2 g. It was obtained as colourless crystals from hot water, m. p. 185-86° (decomp.). (Found : C, 22·6 ; H, 4·6 ; N, 13·2. $C_4H_{10}O_8N_2$ requires C, 22·4 ; H, 4·7 ; N, 13·1 per cent).

Diethylanil-alloxan.—To diethylaniline (16·4 g.) heated on a steam-bath and mechanically stirred, a strong hot aqueous solution of alloxan (16 g.) was added dropwise, when the mixture assumed a pink colouration and crystals gradually began to separate. After standing for 48 hours, the mixture was filtered, the solid washed with water and alcohol and dried, yield 22·3 g. It is insoluble in water but soluble in hot alcohol, from which it crystallises as colourless crystals, m. p. 194-95° (decomp.). (Found : C, 57·9 ; H, 5·7 ; N, 14·3. $C_{14}H_{17}O_4N_3$ requires C, 57·7 ; H, 5·8 ; N, 14·4 per cent).

p-*Diethylaminobenzylidene*-p-*aminodimethylaniline.* — Diethylaniline (5 g.), dissolved in concentrated hydrochloric acid (32%, 10 c. c.) was added to a cold solution of formaldehyde (40%) and the mixture heated on a boiling water-bath for 15 minutes. Powdered *p*-nitrosodimethylaniline hydrochloride (5 g.) was then added. After a vigorous reaction the red solution was diluted with water (60 c. c.) and made alkaline with cold sodium carbonate solution (10%, 65 c. c.). After allowing to stand for 36 hours, the dark brown precipitate was filtered, washed with a mixture of alcohol and ether (1 : 1) and dried, yield 6·9 g. For further purification the compound was dissolved in alcohol and reprecipitated with water. It was obtained as greenish yellow crystals, m.p. 144-45°. (Found : C, 77·1 ; H, 8·5 ; N, 14·1. Calc. for $C_{19}H_{25}N_3$: C, 77·2 ; H, 8·4 ; N, 14·2 per cent).

p-*Diethylaminobenzylidene*-p-*aminodiethylaniline.*—A mixture of diethylaniline (15 g.), formaldehyde solution (40%, 9 c. c.) and concentrated hydrochloric acid (20 c. c.) was heated on a steam-bath for 20 minutes. To the hot mixture freshly prepared *p*-nitrosodiethylaniline (6 g.) was added all at once. After the initial reaction had subsided, the solution was diluted with water to 200 c.c. and 15% caustic soda solution added until the red colour disappeared. The precipitated benzylidene compound was filtered, washed with dilute alcohol, crystallised from methyl alcohol, m. p. 147-49°. (Found : C, 78·4 ; H, 9·1 ; N, 12·8. $C_{21}H_{29}N_3$ requires C, 78·0 ; H, 8·9 ; N, 13·0 per cent).

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Received July 8, 1936.

Removal of Antimony from its Solutions by Nitric Acid.

BY M. B. RANE, K. KONDAIAH AND M. K. RATNAM.

The determination of the solubilities in aqueous nitric acid of various concentrations of Sb_2O_3, Sb_2O_4, Sb_2O_5 and of the residue left when antimony salts are treated repeatedly with strong HNO_3, was undertaken with a view to find out how far antimony could be completely removed from its solutions by treatment with HNO_3.

Antimony in each of the extracts was determined by the usual bromate method. The residue (*cf.* columns 5 and 6 of the table) was analysed for antimony by Sn and HCl method, and water by absorption in $CaCl_2$ tubes and was found to be $Sb_2O_5, 2H_2O$, when dried at 120° and $3\ Sb_2O_5, 2H_2O$ when dried at 160°.

HNO_3 conc.	Antimony oxide in a litre of the acid extract at 100°			Sb_2O_5 in a litre of the acid extract at 100° of the residue dried	
	Sb_2O_3	Sb_2O_4	Sb_2O_5	at 120°	at 160°
1 *N*	647·15 mg.	146·28 mg.	256·5 mg.	359·10 mg.	297·50 mg.
2	739·60	126·78	153·9	307·80	128·25
4	1119·40	48·76	56·4	241·10	97·47
6	1479·20	19·50	20·5	35·91	30·78
8	1294 30	Nil	Nil	5·03	Nil
10	1294·30	"	"	Nil	"
12	1294·30	"	"	"	"
16	1201·85	"	"	"	"

From the above table, it will be seen that Sb_2O_4 and Sb_2O_5 remain practically insoluble in HNO_3 of concentration above 6*N*; even Sb_2O_3 is but sparingly soluble. The residue, too, whether dried at 120° or at 160° is not dissolved by HNO_3 above 8*N*. It is clear, therefore, that antimony can be quantitatively removed by repeated treatment and extraction with concentrated HNO_3 and the method can be utilised for separating tin and antimony together from other bases as insoluble oxides in qualitative analysis.

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BENARES.

Received April 4, 1936.

A Note on the Estimation of Formic Acid in Commercial Acetate of Lime.

BY S. D. SUNAWALA.

The gravimetric method described by Auerbach and Zeglin (*Z. physikal. Chem.*, 1922, **103**, 167) and the volumetric method suggested by Fouchet (*Bull. Soc. chim.*, 1912, **11**, 323) for the estimation of formic acid, when in aqueous or in acetic acid solutions, were found to give accurate results.

In the case of commercial acetate of lime, however, after decomposing the sample by the method of Fresenius (*J. Soc. Chem. Ind.*, 1908, **27**, 1012), the volumetric method was found to give unreliable results, due to the presence of higher fatty acids and pyroligneous matter in the distillate which hindered the correct end-point of the titration. The gravimetric method on the other hand, gave much more concordant and satisfactory results, and under the present existing methods of estimation, should be preferred.

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Review

The Structure of Metals and Alloys.—BY WILLIAM HUME-ROTHERY, M.A., D.SC., OXFORD UNIVERSITY. INSTITUTE OF METALS MONOGRAPH AND REPORT SERIES, NO. 7, 1936. Pp. 120.

With the aid of X-ray method of Crystal analysis within the last few years a considerable progress has been made in developing a theory of the structure of metals and alloys. This has resulted in bringing some order into the chaotic state of knowledge, which we had hithertofore, regarding the structure of this class of substances.

The book under review is a monograph on the subject written by one who is already well known as an authority in this branch of study, and as such the book has a special significance and value of its own.

The book consists of six parts. Part I deals briefly with the structure of atoms, molecules and crystals, this is followed by the crystal structure of the elements in Part II. The importance of atomic radii in determining the structure of metallic crystals is discussed in Part III.

In Part IV, the influence of factors like the atomic size and valency on the formation of primary solid solution has been clearly dealt with. A description of the form of liquidus and solidus curves is given in this section. Finally, the conditions for the formation of superlattice structures have been discussed.

The structure of intermetallic compounds forms the subject matter of Part V of the book. Normal valency compounds, electron compounds and the electron concentration rule are discussed here.

The last part (VI) deals with the imperfections in crystals and deviations from the ideal lattice. The theory of "*mosaic structure*" has been critically examined in this connection.

The monograph is a valuable review on the subjects dealt with; and the lists of references are complete and up-to-date.

The book should be possessed and read by all those who are workers in, or students of, this interesting branch of study. Further, it can be strongly recommended to all advanced students of inorganic and metallurgical chemistry.

P. R.

On the Physico-chemical Properties of Electrodialysed Gels of Silica, Alumina, Ferric Hydroxide and their Mixtures. Part II. Moisture Retention Capacity of the Gels Saturated with Different Cations.

By Promode Behari Bhattacharyya and Kalipada Ganguly.

In a previous paper of this series (*J. Indian Chem. Soc.*, 1936, **13**, 204) the ion exchange properties of the above synthetic gels, which are probable constituents of soil, have been described. In the present investigation their property of absorbing and retaining water vapour under conditions of varying aqueous tensions, have been studied. The results have a bearing on the property of moisture retention by soil colloids, a subject which has evoked considerable interest in recent years. Notable contributions in this direction have been made, amongst others, by Anderson (*J. Agric. Res.*, 1929, **38**, 565), Puri, Crowther and Keen (*J. Agric. Sci.*, 1925, **15**, 86), Parker ane Pate (*J. Amer. Soc. Agron.*, 1926, **18**, 470), Thomas (*Soil Sci.*, 1928, **25**, 485) and Baver (*J. Amer. Soc. Agron.*, 1928, **20**, 921).

The property of silica gel to absorb water vapour is well known. The recent investigations of Urquhart (*J. Textile Inst.*, 1929, **20**, 117), Lambert (*Proc. Roy. Soc.*, 1931, **A134**, 246) and Pidgeon (*Canadian J. Res.*, 1934, **10**, 713) have definitely established a hysteresis effect characterising the phenomenon. Puri, Crowther and Keen (*loc. cit.*) obtained evidence of a similar hysteresis effect in the case of soil colloids. Under the experimental conditions of this work it has not been possible to study the nature of the hysteresis loop, the main object of this investigation being to study the variation of the moisture retention capacity of the gels depending on their composition and the nature of the cations saturating them.

EXPERIMENTAL.

The methods of preparing the gels and saturating them with various cations have been described in the previous part (*loc. cit.*).

The following sulphuric acid-water mixtures were prepared to correspond to different V. P. (extrapolated from the figures given in Landolt Börnstein Tabellen, 5 Auflage II, p. 1935).

Temp. 34°.

	1	2	3	4	5
Acid (%) ...	23·0	42·0	55·8	62·2	81·1
V. P. (mm.) ...	33·63	21·38	10·25	6·20	0·55

Five desiccators, each containing sulphuric acid of a particular strength, were maintained at a constant temperature of 34° in an electrically regulated thermostat.

The method of saturation with water vapour was similar to that followed by Puri, Crowther and Keen (*loc. cit.*). About 5 g. portions of each gel were used for each set of experiment, the gel being transferred from a more humid atmosphere to that of next lower humidity. The amount of moisture retained by these gels was determined by igniting the gel after the constant weight had been reached in the lowest humid atmosphere. Generally 72 hours were sufficient to reach the equilibrium at a given vapour pressure.

TABLE I*a*.

Water absorption.

H_2O (in g.) per g. of the ignited oxide at 34° over

The cation with which the gel has been saturated.	23·0% acid. V.P. = 33·625 mm.	55·8% acid. V.P. = 10·25 mm.	81·1% acid. V.P. = 0·55 mm.	23·0% acid. V.P. = 33·625 mm.	55·8% acid. V.P. = 10·25 mm.	81·1% acid. V.P. = 0·55 mm.	23·0% acid. V.P. = 33·625 mm.	55·8% acid. V.P. = 10·25 mm.	81·1% acid. V.P. = 0·55 mm.
	SiO_2			Al_2O_3			Fe_2O_3		
Na	0·3852	0·1672	0·0710	0·5541	0·5160	0·4611	0·2261	0·1630	0·0910
K	0·3395	0·1273	0·0415	0·5300	0.4950	0·4412	0·1678	0·0990	0·0421
Ca	0·4726	0·1428	0·0312	0·5320	0·4990	0·4360	0·1665	0·1080	0·0532
Mg.	0·4174	0·1543	0·0512	0·5250	0·4980	0·4392	0·2513	0·1586	0·0715

TABLE I*b*.

Sample taken.	Substituted cation.	H_2O per g. of the ignited mixture at 34°. 23% acid. V.P. = 33·625 mm.	42% acid. V.P. = 21·357 mm.	55·8% acid. V.P. = 10·25 mm.	62·2% acid. V.P. = 6·20 mm.	81·1% acid. V.P. = 0·55 mm.
$SiO_2-Al_2O_3$ Mixture (I)	Na	0·606 g.	0·501 g.	0·343 g.	0·293 g.	0·182 g.
	K	0·635	0·531	0·375	0·334	0·225
$\frac{\text{Mol. } SiO_2}{\text{Mol. } Al_2O_3} = 4·37$	Ca	0·620	0·512	0·357	0·305	0·200
	Mg	0·629	523	0·371	0·330	0·239
$SiO_2-Al_2O_3$ Mixture (II)	Na	0·937	...	0·821	...	0·442
	K	0·709	...	0·616	...	0·284
$\frac{\text{Mol. } SiO_2}{\text{Mol. } Al_2O_3} = 1·33$	Ca	0·743	...	0·648	...	0·284
	Mg	0·666	...	0·560	...	0·276
$SiO_2-Fe_2O_3$ Mixture (III)	Na	0·549	0·322	0·219	0·193	0·131
	K	0·589	0·337	0·215	0·189	0·130
$\frac{\text{Mol. } SiO_2}{\text{Mol. } Fe_2O_3} = 3·68$	Ca	0·545	0·327	0·220	0·198	0·139
	Mg	0·588	0·331	0·220	0·194	0·134
$SiO_2-Fe_2O_3$ Mixture (IV)	Na	0·453	...	0·424	...	0·152
	K	0·461	...	0·435	...	0·161
$\frac{\text{Mol. } SiO_2}{\text{Mol. } Fe_2O_3} = 1·04$	Ca	0·488	...	0·463	...	0·191
	Mg	0·501	...	0·474	...	0·192

TABLE II.

Sample taken.	Substituted cation.	H_2O per g. of the ignited mixture (calculated from the law of additive mixture). V.P. = 33·62 mm.	V.P = 10·25 mm.	V.P. = 0·55 mm.
Mixture (I)	Na	0.4301 g.	0·2647 g.	0·1802 g.
	K	0·3905	0·2303	0·1532
	Ca	0·48 0	0·2425	0·1446
	Mg	0·4453	0·2505	0·1598
Mixture (II)	Na	0·4798	0·3625	0·2894
	K	0·4462	0·3332	0·2653
	Ca	0·5058	0·3423	0·2579
	Mg	0·4776	0·3468	0·2683
Mixture (III)	Na	0·3178	0·1654	0·0794
	K	0·2669	0·1154	0·0417
	Ca	0·3432	0·1282	0·0404
	Mg	0·3470	0·1561	0·0604
Mixture (IV)	Na	0·2706	0·1642	0·0854
	K	0·2159	0·1070	0.0419
	Ca	0·2522	0·1177	0·0470
	Mg	0·2978	0·1574	0·0681

DISCUSSION.

Table I gives the amounts of moisture retained by the different samples at various vapour pressures. A good correlation has often been found between the moisture retention capacity of a soil and the nature of the cation with which it has been saturated. Thus Gedroiz (*Zhur. Opyt. Agron.*, 1914, **15**, 205), Smolik (*Bull. Chechos. Acad. Agric.*, 1930; *Proc. Internat. Soc. Soil Sci., abst.*, 1930, **5**, 159) and Perkin and King (*Soil Sci.*, 1931, **32**, 409) observed that a maximum amount of moisture was retained when Na was the saturating cation. This is to be expected from theoretical considerations as the Na- ion, being heavily hydrated, is most likely to increase the affinity of the gel surface for water vapour. Indications, however, exist in the literature showing that the moisture retention capacity is not simply determined by the nature of the saturating cation. Thus the results of Anderson (*loc. cit.*), Parker and Pate (*loc. cit.*), and Baver (*loc cit.*) do not bear out the above characteristic effect of sodium ions regarding moisture retention by soil colloids saturated with them.

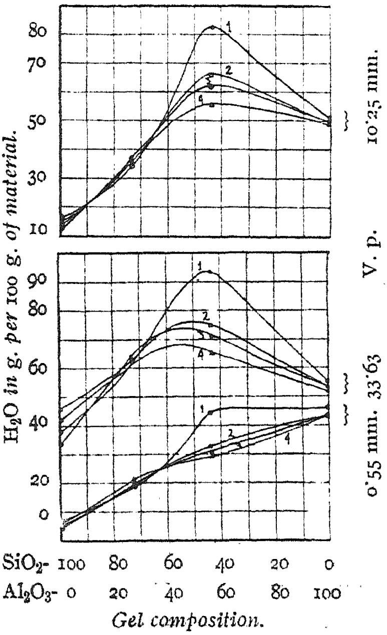
The results given in the previous section show that besides the usual effect of the cation, the composition of the gel is an important factor in determining its moisture retention capacity. Na-saturated alumina absorbs more water vapour than the same gel saturated with the cations K, Ca or Mg (*cf.* Tables I*a* and I*b*). The difference becomes still more marked in mixtures of alumina and silica. In the case of the pure ferric hydroxide gel also maximum moisture retention capacity is observed when Na is the saturating cation. In the case of silica-ferric hydroxide gels, however, the order of the various cations in respect of moisture retention depends in a peculiar manner on the composition of the gel and at a certain composition the order is reversed compared with that obtained in the case of the pure ferric hydroxide gel, *e.g.*, Mg-saturated sample shows the highest moisture retention capacity.

The results also indicate that an important factor in determining the order of the cations regarding the amount of water vapour absorbed is the vapour pressure at which the experiment has been carried out.

It is interesting to note that as silica is added to the sesquioxides, their moisture retention capacity gradually increases, reaches a maximum and again decreases, giving small values of moisture absorption with pure silica. The maximum in case of silica-alumina mixture is at the gel composition 45% SiO_2 and 55% Al_2O_3; the molar ratio of SiO_2, Al_2O_3 being 1·4. The composition of SiO_2—Fe_2O_3 mixture at its maximum moisture retention capacity is about 35% SiO_2 and 65% Fe_2O_3. It is curious to note that the ratio SiO_2/Fe_2O_3 is also about 1·4.

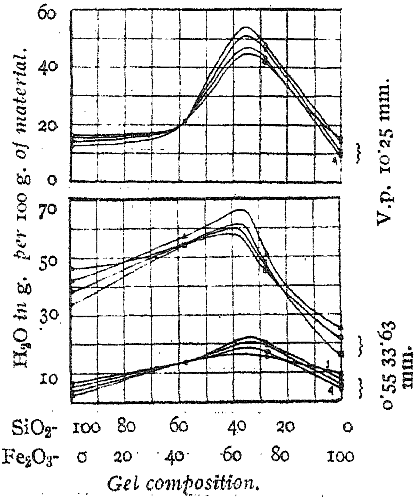
Another interesting point emerges from these data. The effect of of substitution of cations on the various samples is most marked at a certain range of composition of the complex. Thus in case of SiO_2—Al_2O_3 mixture, the most marked range is between the ratios 2·6 and 0·5. In case of SiO_2—Fe_2O_3 mixture also, the most marked range is between the ratios 2·6 and 0·5.

FIG. 1*a*.



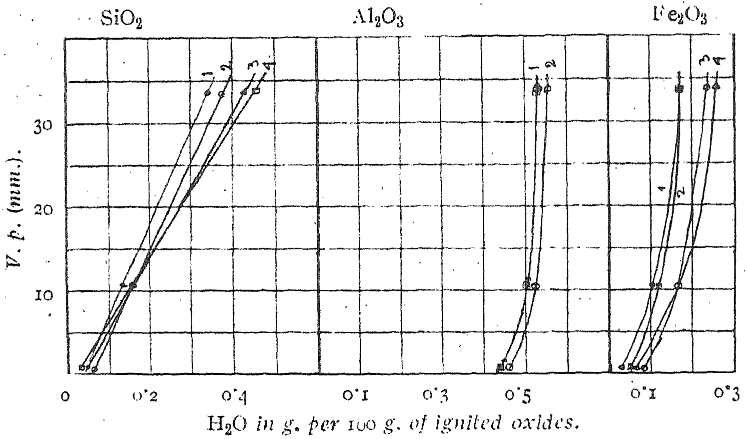
Curves 1-4 refer respectively to Na, Ca, K, and Mg-saturated materials.

FIG. 1*b*.



The relation between the vapour pressure and moisture retention capacity of our synthetic materials are shown in Fig 1. In our experiments, the water absorption curve of the gels were obtained up to a vapour pressure limit of 34 mm. The foams of the curves are similar to those of Puri, Crowther and Keen (*loc. cit.*).

FIG. 2a.



Curves 1—4 (SiO_2) refer respectively to K, Na, Mg and Ca-saturated
,, ,, (Fe_2O_3) ,, ,, K, Ca, Na and Mg ,,

FIG. 2b.

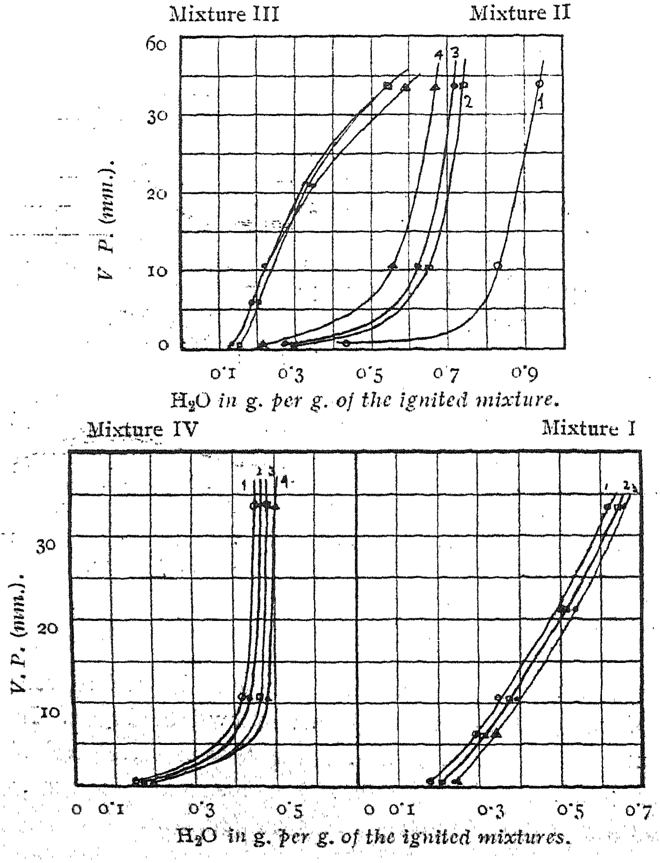
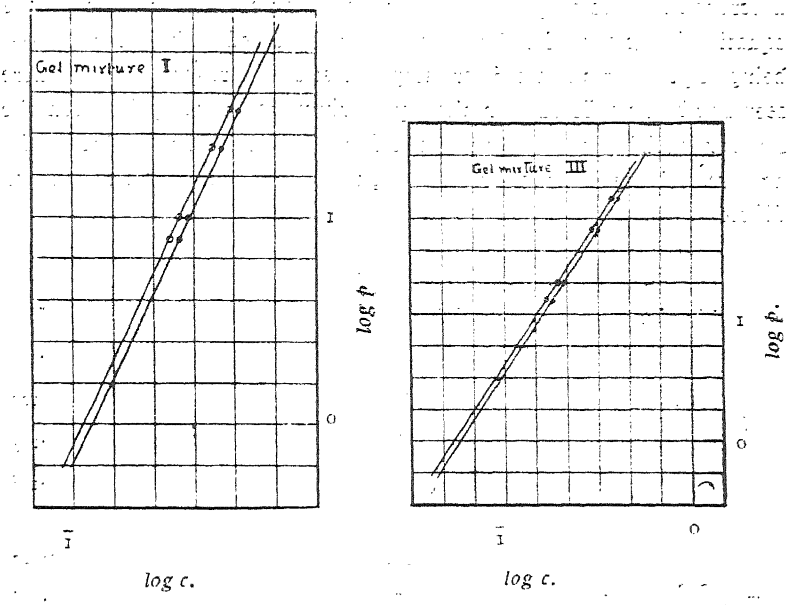


FIG 3.



Comparing Table II with Table I, it will be noted that the moisture retention capacity of the mixed silica-sesquioxide gels is far greater than that calculated from the law of mixtures. It is remarkable that the base exchange capacity of silica-sesquioxide gels is also always greater than that calculated from the law of mixtures (*cf.* the previous paper of this series). As the affinity of the surface for a metal ion increases, the moisture retention capacity also increases.

In Fig. 3 are plotted the log $c - \log p$ curves for mixtures I and III. Considering the equilibrium relationship from the stand point of Freundlich's equation

$$c = Kp^{\frac{1}{n}}$$

one would expect a straight line for the log c-log p curve. The figures show that all the points, with the exception of the one at the lowest humidity, lie in a straight line. The divergence at low humidities is apparently due to some moisture being held in chemical combination. It may be noted that the amount of water held by these gels by chemical combination is much smaller than the amount necessary for these gels to exist entirely as H_2SiO_3, $Al(OH)_3$, or $Fe(OH)_3$.

The log c —log p curves for the same material substituted with different bases are all parallel. Hence the values of n in the above equation is the same for the same material treated with various bases, being equal to 2·3 and 1·6 for samples I and III respectively. There seems to be no difference in the equilibrium relationship between the same material treated with the different bases. The value of K, however, changes, although very slightly, with the substitution of different bases.

TABLE III.

Mixed gel.	Substituted base.	K.
(I) $\frac{SiO_2}{Al_2O_3} = 4{\cdot}37$	Na	0·112
	K	0·120
	Ca	0·115
	Mg	0·118
(II) $\frac{SiO_2}{Fe_2O_3} = 3{\cdot}68$	Na	0·047
	K	0·048
	Ca	0·047
	Mg	0·048

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Denitrification in Sunlight and its Retardation.
Part III.

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In previous publications it has been shown that the loss of nitrogen in the gaseous state takes place in the soil when nitrogenous compounds undergo nitrification in the soil. When the amounts of nitrogenous compounds present or added to the soil are large and the conditions are favourable for their rapid nitrification, there is marked loss of nitrogen in the gaseous state. This type of nitrogen loss, which occurs when the conditions are favourable for oxidation and nitrification of the nitrogenous compounds, was systematically studied by Lipman and Blair (*Soil Sci.*, 1921, **12**, 1) and emphasised by Russell ("Soil Conditions and Plant Growth," 1932, pp. 367-369) has been satisfactorily explained by Dhar and Mukerji (*Nature*, 1934, **134**, 572; *J. Indian Chem. Soc*, 1935, **12**, 67, 756). This denitrification is very prominent in tropical countries where due to the high temperature and sunlight, the nitrification is greatly facilitated.

In several publications we have shown that the nitrification of ammonium salts is greatly accelerated by sunlight. In the present communication, the influence of sunlight on the velocity of nitrification of ammonium sulphate and the nitrogen loss consequent on nitrification have been studied, under field conditions, by applying known amounts of ammonium sulphate to plots of lands in the University compound. In order to exclude light, plots of lands to which ammonium sulphate was added, were completely covered with wooden planks. The covered and the uncovered plots were dug up once in ten days for improving their æration and the conditions of the plot were identical except the ones covered did not receive sunshine. The ammonium sulphate, which was used in these experiments, was dissolved in water and spread over the experimental plots, as uniformly as possible. From time to time soil samples were taken out and the ammoniacal, nitric total nitrogen and carbon were estimated. The following are the experimental results :—

TABLE Ia.

1080 G. of $(NH_4)_2SO_4$ per 36 sq. ft., *i.e.*, 138·6 kg. of N as $(NH_4)_2SO_4$ per acre of land used.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Uncovered	0·032%	0·0028%	0·0348%	0·14%	0·476%	18th Jan., 1936
Covered	0·0373	0·004	0·0413	0·148	0·48	,,
Uncovered	0·008	0·00934	0·01734	0·1081	0·481	30th Jan., 1936
Covered	0·032	0·0056	0·0376	0·1382	0·481	,,
Uncovered	0·00582	0·01132	0·0174	0·1032	0·478	19th Feb., 1936
Covered	0·0224	0·0082	0·0306	0·1328	0·478	,,
Uncovered	0·00504	0·01194	0·01698	0·0995	0·478	9th Mar., 1936
Covered	0·02176	0·0092	0·031	0·1324	0·472	,,
Uncovered	0·00416	0·01224	0·0164	0·0982	0·478	4th Apr., 1936
Covered	0·0211	0·00976	0·0308	0·1312	0·478	,,
Uncovered	0·00324	0·01302	0·01636	0·0921	0·478	25th Apr., 1936
Covered	0·0185	0·01144	0·0299	0·1308	0·478	,,

TABLE Ib.

2160 G. of $(NH_4)_2SO_4$ per 36 sq. ft., *i.e.*, 277·2 kg. of N as $(NH_4)_2SO_4$ per acre of land used.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Uncovered	0·0468%	0·0028%	0·0496%	0·200%	0·476%	18th Jan., 1936
Covered	0·0624	0·004	0·06664	0·2	0·482	,,
Uncovered	0·0234	0·01468	0·03808	0·167	0·481	30th Jan., 1936
Covered	0·05	0·0048	0·0548	0·1902	0·482	,,
Uncovered	0·02	0·0148	0·0348	0·1425	0·478	19th Feb., 1936
Covered	0·0442	0·00844	0·0526	0·1842	0·478	,,
Uncovered	0·01844	0·01544	0·03388	0·1325	0·478	9th Mar., 1936
Covered	0·0425	0·00936	0·0518	0·1841	0·478	,,
Uncovered	0·01784	0·0157	0·03354	0·1281	0·472	4th Apr., 1936
Covered	0·04024	0·01036	0·0508	0·1834	0·478	,,
Uncovered	0·00862	0·01848	0·0271	0·1122	0·472	25th Apr., 1936
Covered	0·03824	0·01242	0·0506	0·1832	0·472	,,

These experimental results show definitely that the nitrification of ammonium sulphate is much quicker in the plots receiving sunshine than in those which are covered with wooden planks. Moreover, in the uncovered plots there is more nitrogen loss than in the covered plots. Thus when 131·6 kg. of nitrogen were added to the soil, the loss in nitrogen in the uncovered plots amounted to 34·2% in about 3 months, whereas in the covered plots the loss is only 11·6%. Similarly with 277·2 kg. of nitrogen added per acre of soil, the loss is 43·9% in the uncovered and 8·6% in the covered plot. These results conclusively prove that in presence of sunlight, ammonium sulphate is nitrified at a much greater velocity than in the dark. Along with the greater velocity of nitrification in sunlight, there is a concomitant greater loss of nitrogen in sunlight than in the dark. These results obtained in field trials strongly support our conclusion, that sunlight plays an important part in the nitrification and in denitrification in tropical countries. As the plots were not watered and as there were no showers in the months in which the experiments were carried on, the question of the passing of the nitrogen into the subsoil does not arise.

We have already emphasised that this type of denitrification, when the conditions are favourable for oxidation and nitrification of the nitrogenous compounds in the soil, is caused by the formation and decomposition of NH_4NO_2 in the process of nitrification. The formation of ammonium nitrite from ammonium salts and proteins, require oxygen, and that is why, this type of denitrification is facilitated by increased soil æration. In the process of nitrification, the ammonium ion is replaced first, by the acidic NO_2-ion and finally by NO_3-ion and hence in the process of nitrification, the acidity of the system increases. It is well known that nitrous acid decomposes according to the equation

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

Moreover, acids have been found to facilitate the thermal and photochemical decomposition of ammonium nitrite, which is temporarily formed in the soil in the process of nitrification. Also Murty and Dhar (*J. Indian Chem. Soc.*, 1930, 7, 985) have shown that sunlight or artificial light markedly accelerates the decomposition of nitrous acid according to the above equation. All these factors are responsible for the nitrogen loss from soils, when ammonium salts or proteins added or present in the soil undergo nitrification. Moreover, as the soils become slightly acidic on the addition of ammonium sulphate, the loss of nitrogen from such soils cannot be due to the escape of gaseous ammonia.

In previeus papers it has been emphasised that the presence of carbonaceous substances like carbohydrates, fats, etc. present in the soil along with the nitrogenous substances, retard the nitrogen loss from soils. It has been shown by us that in presence of the carbonaceous substances, the velocity of nitrificatfon of the nitrogenous compounds is decreased and consequently the nitrogen loss is concomitantly decreased. The following field trials with the addition of $(NH_4)_2SO_4$ to the soil, with or without molasses, show definitely that molasses retard the velocity of nitrification and denitrification in soils.

TABLE II*a*.

1080 G. of $(NH_4)_2SO_4$ per 36 sq. ft., *i.e.*, 138·6 kg. of N as $(NH_4)_2SO_4$ per acre of land used and 2·5 kg. molasses per 36 sq. ft.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Unmolassed	0·032%	0·0028%	0·0348%	0·14%	0·476%	18-1-36
Molassed	0·032	0·0028	0·0348	0·14	0·743	„
Unmolassed	0·008	0·00934	0·01734	0·1081	0·481	30-1-36
Molassed	0·0112	0·00972	0·02092	0·1179	0·745	„
Unmolassed	0·00582	0·01132	0·01714	0·1033	0·478	19-2-26
Molassed	0·010	0·010	0·02	0·1185	0·744	„
Unmolassed	0·00504	0·01194	0·01698	0·0995	0·478	9-3-36
Molassed	0·00984	0·0102	0·02	0·1172	0·744	„
Unmolassed	0·00416	0·01224	0·0164	0·0982	0·478	4-4-36
Molassed	0·00956	0·01048	0·02	0·1092	0·742	„
Unmolassed	0·00324	0·01302	0·01626	0·09212	0·478	25-7-36
Molassed	0·00896	0·01104	0·02	0·1012	0·742	

TABLE II*b*.

2160 G. of $(NH_4)_2SO_4$ per 36 sq. ft., *i.e.*, 277·2 kg. as $(NH_4)_2SO_4$ per acre of land used and 2·5 kg. of molasses per 36 sq. ft. of land.

Condition.	NH_3-N.	Nitric-N.	Available N.	Total N.	Total C.	Date of analysis.
Unmolassed	0·0468%	0·0028%	0·0496%	0·2%	0·476%	18-1-36
Molassed	0·0468	0·0028	0·0496	0·2	0·743	,,
Unmolassed	0·0234	0·01468	0·0380	0·167	0·481	30-1-36
Molassed	0·029	0·01504	0·044	0·1866	0·745	,,
Unmolassed	0·020	0·01488	0·0348	0·1425	0·478	19-2-36
Molassed	0·0294	0·01510	0·0455	0·1788	0·744	,,
Unmolassed	0·01844	0·01544	0·03388	0·1325	0·478	9-3-36
Molassed	0·02774	0·01462	0·0445	0·1725	0·744	,,
Unmolassed	0·01784	0·0157	0·03354	0·1281	0·472	4-4-36
Molassed	0·0248	0·0164	0·0412	0·17	0·743	,,
Unmolassed	0·00862	0·01848	0·0271	0·1122	0·472	25-4-36
Molassed	0·01856	0·02024	0·0388	0·1642	0·742	,,

Thus with 138·6 kg. of nitrogen as ammonium sulphate per acre of land, the loss of nitrogen amounts to 34·2% in the absence of molasses, whilst with molasses it is 27·1%. With 277·2 kg. of nitrogen, the loss is 43·9% without molasses. With molasses the loss is only 17·9%.

It will be clear, therefore, that the value of ammonium sulphate as a manure to be used in tropical countries should be greatly enhanced, if it is mixed with molasses, fats or any other carbonaceous material. Oil-cakes containing fats and nitrogenous compounds ought to be effective in tropical countries for fats are known to retard the oxidation and nitrification of the nitrogenous compounds in the soil. It is clear, why farmyard or green manure, produces better crop yield than ammonium sulphate alone, because the carbonaceous substances present in the farmyard or green manure, retard the nitrification of the nitrogenous compounds present in the soil and decrease the nitrogen loss. As a matter of fact, when farmyard manure is added to the soil more nitrogen is conserved in the soil than with ammonium sulphate. This is evident from the following important results obtained from the Rothamsted fields:—

	Total N.
1. Receiving no manure since 1843	0·095%
2. Receiving farmyard manure since 1852	0·256
3. Receiving complete artificials $(NH_4)_2SO_4$	0·099
4. Receiving complete farmyard manure	0·253
5. Receiving potash and phosphate but no nitrogen	0·090

Apart from this influence of the carbonaceous substances like sugars, cellulose, fats, etc., on the conservation of soil nitrogen, these substances when added to the soil along with farmyard or green manure, or straw, also leads to the fixation of atmospheric nitrogen in the soil. Hence the carbonaceous substances, like sugars, cellulose, fats, etc. added to the soil are not only effective in nitrogen conservation, but cause nitrogen fixation as well.

It is of interest to note that after six or seven months, the plots containing ammonium sulphate alone are feebly acidic (p_H 6·9 to 6·6), whilst the plot containing ammonium sulphate and molasses show p_H 7 to 7·2.

In a previous paper (*J. Indian Chem. Soc.*, 1935, **12**, 756) it has been shown that an aqueous solution of ammonium nitrite kept at 40° or 50° decomposes appreciably, when exposed to the total light of a gas-filled tungsten filament lamp of 1000 watt. We have investigated the decomposition of ammonium nitrite when illuminated by the same light or in the dark, when the solutions are maintained at 20° or 30°. The following are the experimental results.

TABLE IIIa.

NH_3-N added as $(NH_4)_2SO_4$=0·14 g. NO_2-N added as $Ba(NO_2)_2$=0·15 g. Total N added=0·29 g. in 20 c.c. of solution.

LIGHT.

Exposure at	NH_3-N left.	NO_2-N left.	Total N left.	NH_3-N lost.	NO_2-N lost.	Total N lost.	% lost
30° for 5 hours	0·1343	0·1422	0·2786	0·0059	0·0058	0·0114	3·9
30° ,, 10 ,,	0·1272	0·135	0·2642	0·0128	0·013	0·0258	8·2
30° ,, 20 ,,	0·112	0·12	0·234	0·028	0·028	0·056	19·6
20° ,, 5 ,,	0·14	0.148	0·288	nil	nil	nil	nil
20° ,, 10 ,,	0·1312	0·14	0·271	0·0088	0·0088	0·019	6·5
20° ,, 20 ,,	0·123	0·132	0·257	0·017	0·016	0·033	11·3
20° ,, 40 ,,	0·1152	0·1248	0·2402	0·0248	0·0232	0·0498	17

DARK.

Kept at	NH_3-N left.	NO_2-N left.	Total N left.	NH_3-N lost.	NO_2-N lost.	Total N lost.	% lost
30° for 5 hours	0·14	0·148	0·288	nil	nil	nil	nil
30° ,, 10 ,,	0·1372	0·1452	0·2855	0·0028	0·00275	0·0045	0·1
30° ,, 20 ,,	0·1327	0·14	0·2754	0·0073	0·008	0·0146	5
20° ,, 5 ,,	0·14	0·148	0·29	nil	nil	nil	nil
20° ,, 10 ,	0.14	0·148	0·29	nil	nil	nil	nil
20° ,, 20 ,,	0·14	0·148	0·29	nil	nil	nil	nil
20° ,, ,,	0·1318	0·14	0·2729	0·0082	0·008	0·0171	5·7

TABLE III *b*.

Treatment after.	Loss of nitrogen			Percentage loss in	
	Dark and light.	Dark only.	Light only.	Dark.	Light.
5 hrs. at 30°	0·01149	nil	0·01149	nil	3·9
10 hrs. at 30°	0·02589	0·0045	0·0213	0·1	8·1
20 hrs. at 30°	0·056	0·0146	0·0414	5·0	14·6
5 hrs. at 20°	nil	nil	nil	nil	nil
10 hrs. at 20°	0·019	nil	0·019	nil	6·5
20 hrs. at 20°	0·033	nil	0·033	nil	11·3
40 hrs. at 20°	0·0498	0·0171	0·0327	5·7	11·5

The foregoing results show that at 39°, an aqueous solution of ammonium nitrite containing 14·5 g. of nitrogen per litre undergoes slight decomposition into nitrogen and water even in the dark. Light markedly accelerates this decomposition. At 20°, the thermal decomposition is very slight but in presence of light, the decomposition is appreciable. Hence in the soil, ammonium nitrite formed in the process of nitrification of nitrogenous compounds can decompose into gaseous nitrogen in the day time even when the soil temperature does not exceed 20°. That is why, marked nitrogen loss had been observed in heavily manured fields in Rothamsted and other experimental stations.

SUMMARY.

1. Field trials show, that nitrification of ammonium sulphate is much quicker in plots receiving sunlight, than in those covered with wooden planks. Moreover, in the uncovered plots there is more nitrogen loss than in the covered ones. Thus with 277·2 kg. of nitrogen added as ammonium sulphate per acre of land, the loss is 43·9% in the uncovered and only 8·2% in the covered plot.

2. Molasses appreciably decrease the velocity of nitrification of ammonium sulphate added to fields and also retards nitrogen loss. Thus with 277·2 kg. of nitrogen per acre of land, the loss is 43·9% with molasses and without molasses the loss is 17·9%.

3. Carbonaceous substances like sugars, cellulose, fats etc. not only conserve soil nitrogen by decreasing the velocity of nitrification and denitrification, but also cause nitrogen fixation in the soil as well.

4. An aqueous solution of ammonium nitrite containing 14·5 grams nitrogen per litre undergoes appreciable decomposition into gaseous nitrogen and water at 20° and 44° even in the dark. The total light from a tungsten filament lamp of 1000 watt accelerates the thermal decomposition of ammonium nitrite. This observation explains why marked nitrogen loss has been observed in heavily manured fields at Rothamsted and other experimental stations.

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Investigations on Cod Liver Oil Emulsions. Antagonism of Emulsifying Agents.

By Nirmalapada Chatterjee.

It is well known that there are two types of emulsions, one oil in water, the other water in oil emulsion. For each type of emulsion, there are characteristic emulsifiers which promote the formation of only one type of emulsion. Thus, alkali metal soaps, gum acacia, lecithin, etc., produce O-W emulsion and calcium soap, cholesterol, carbon powder, etc., produce W-O emulsion. When emulsifiers producing opposite types of emulsions are mixed together, their mutual effect is antagonistic. The type of the emulsion depends on the relative wetting power of the two phases, oil and water, with respect to the emulsifying agent and on the surface potential of the membrane between the two phases.

Apart from the antagonistic effect leading to reversal of phases, there are cases of antagonism amongst emulsifiers which individually produce the same type of emulsion, but when these are mixed together they break the emulsion. Such cases have, however, drawn little attention uptil now and the mechanism of such effects is very little understood. There are only a few stray cases mentioned in the literature.

In the course of investigation on the preparation of emulsion of Cod Liver Oil for pharmaceutical purposes several interesting cases of the above type of antagonism of emulsifiers were observed. Most striking results were obtained with bile salts and gum acacia. Both bile salts and gum acacia when present alone, produce stable O-W emulsion; but when these are present together the emulsion does not form at all. In the cases of turkey-red oil, lecithin and sodium oleate, it was found that when mixed with gum acacia, the emulsion formed liberates oil slowly at the top although when gum acacia is present alone, no such separation is observed. Gelatin, egg-albumin, saponin, Irish mess, agar agar and gum tragacanth when mixed with gum acacia, instead of causing liberation of oil, stabilise the emulsion to that effect.

EXPERIMENTAL.

Emulsifying agents.

Gum acacia—Merck, extra white fine powder B. P.

Irish moss—Merck. The moss was cut to fine pieces and then boiled with distilled water for one hour. The boiled mixture was kept overnight and then strained through fine muslin cloth.

Gelatin—Merck, Gold lebel. Dissolved in distilled water at 60°.

Egg-albumin—Merck. Dry scales were triturated with oil till finely dispersed.

Turkey-red oil—Prepared in the laboratory from pure castor oil.

Bile salt—Prepared in the laboratory from ox-bile and purified.

Lecithin—Merck. ex ovo.

Sodium oleate—Prepared in the laboratory from reagent quality caustic soda (Merck) and oleic acid (Merck).

Agar agar—White shreds cut into small pieces and then boiled in water to dissolve.

Gum tragacanth—Merck. Albissima.

Saponin.—Merck. Pure white.

In all cases of emulsification, 35 c.c. of pure Norwegian Cod Liver Oil were mixed with 70 c.c. of water. Emulsifiers, like gum acacia, gum tragacanth and egg-albumin were mixed with oil and the other emulsifiers were mixed with water before emulsification. In the case of agar agar, hot solution was employed. On cooling, the emulsion set to a gel. The gel was gently shaken when the normal fluidity was obtained.

Preliminary mixing was done in the mortar and then the coarse emulsion was passed through 'Primier' colloid mill rotating at 3000 r.p.m. at a clearance of 0·003 inch. In all cases the emulsions were passed through the mill three times.

TABLE I.

Emulsions not liberating oil at the top.

Gum acacia.	Irish moss.	Remarks.
0·0%	0·5%	Thick, water separates slowly.
1·0	0·5	Less thick, water separates less slowly.
1·5	0·5	Less thick, water separates rapidly.

TABLE I (contd.).

Gum acacia	Agar agar.	Remarks.
0·0	0·4%	Very thick, coarse, water separates.
1·0	0·4	Thick, less coarse, water separates slowly.
2·0	0·4	Less thick, little or no water separates.
4%	0·4%	Thin, water separates rapidly.
	Traga.	
0	0.4%	Coarse emulsion.
0	0·6	Very thick, coarse.
0	0·8	Coarse, W-O emulsion.
	Gum Traga.	
1	0·4	Less coarse, water separates very slowly.
2	0·6	Do Do Do
4	0·6	Less thick, water separates rapidly.
4	0·8	Thick, water separates very slowly.
	Gelatin.	
0	0·16%	Very thin, water separates rapidly.
1·5	0·08	Do Do
1·5	0·16	Very thin, thickness on keeping, water separates rapidly.
1·5	0·4	Do Do
	Egg-albumin.	
0	0·1%	Very thin, water separates rapidly.
1	0·1	Do Do
1	1·0	Do thickness on keeping.
	Saponin.	
0	0·04%	Very thin, water separates rapidly.
1	0·04	Do Do

With gelatin, egg-albumin and saponin, the consistency was always thin but the particles became finer with increase of concentration of the emulsifiers. With 0·4% gelatin, the emulsion on keeping assumed a curd-like appearance.

TABLE II.

Emulsions where oil separates at the top.

Gum acacia.	Turkey-red oil.	Remarks.
0%	0·75%	Very thin, oil separates slowly from the beginning.
1	1·0	Do Do less Do
	Bile salt.	
0	0·1%	Coarse, very thin, oil separates slowly from the beginning.
0	0·5	Less coarse, Do Do
*0	1·0	Fine, less thin, Do, Do, very slowly, Do
1	0·05	Very thin, oil separates slowly from the beginning.
*1	0·1	Less thin, Do Do
1	0·2	Breaks immediately.
1	0·5	Do
2	0·5	Do
5	0·5	Do
10	1·0	Do
	Lecithin.	
0	0·1%	Very thin, oil separates rapidly.
0	0·5	Less thin Do Do
2	0·1	Do Do
2	0·5	Do oil separates slowly
	Na-oleate.	
0	0·2%	Thin, oil separates slowly.
2	0·2	Do Do

Except in the cases marked with asterisk, all emulsions are thin and water separates at the bottom rapidly.

DISCUSSION.

It is well known that for easy emulsification of the O-W type, the surface tension or the internal viscosity of the dispersion medium should be low. Emulsifiers like sodium oleate, bile salts, turkey-red oil, etc., lower the surface tension and they facilitate emulsification. But emulsions produced by these emulsifiers are not stable over longer periods except under special circumstances. As soon as mechanical or thermal agitation is stopped, the oil globules have a tendency to meet together and accumulate at the top. The film formed on the particles gradually gets thinner and thinner, a direct effect of low surface tension, and ultimately the film ruptures liberating free oil. With emulsifiers like saponin and egg-albumin, the film is not easily broken. These emulsifiers have got a low internal viscosity which facilitates emulsification but the surface tension being high, the film round the oil particles does not easily break. Saponin, as an emulsifier, has this defect that the low internal viscosity of the medium produces a thin emulsion and the covered oil particles float up leaving water at the bottom. Emulsifiers like gum acacia, gum tragacanth, Irish moss, etc., offer high internal viscosity and also high surface tension. Consequently emulsification with these agents is not easily obtained. But once the emulsion is formed the particles can neither coalesce nor float up.

The emulsifiers are classified broadly into three groups : (*i*) Emulsifiers with low internal and superficial viscosity like sodium oleate; (*ii*) Emulsifiers with low internal and high superficial viscosity like saponin; (*iii*) Emulsifiers with high internal and superficial viscosity like gum acacia.

It is evident that although low surface tension enhances adsorption, the adsorbed film is not permanent. To get a permanent film, the adsorbed substances should be irreversibly precipitated at the interface, as was suggested by Ramsden (*Proc. Roy. Soc.*, 1903, **A 72**, 156). Proteid solutions like egg-albumin can be denatured or irreversibly precipitated on air-liquid interface by violent agitation and this type of precipitation produces a permanent coating on an oil-water interface. Addition of salt solutions to the emulsion stabilised with egg-albumin cannot break the film round the oil particle; but the case is just the reverse with films produced by emulsifiers of group (*i*). The difference in the nature of films produced by the emulsifiers of groups (*i*) and (*ii*) is quite evident and it indicates greater stability of film produced by group (*ii*).

Gum acacia, also, has got the property of forming a very tough film round the oil particle and this is evidenced by the fact that when an emulsion is prepared with the help of about 10% of gum acacia, the emulsion even on drying on water-bath does not liberate free oil and the dry mass on moistening with water produces a finely dispersed emulsion.

Our experimental results show that when emulsifiers of group (*i*), which produce low surface tension, are mixed with gum acacia, they hinder the formation of a permanent film and thereby antagonise against the action of gum acacia. Only when the percentage of gum acacia is excessively high so as to supersede the antagonistic effect of low surface tension, we get a stable film.

The effect of bile salts against gum acacia is the most striking. When one per cent of bile salt is used alone, a very finely grained (1 to 5μ) emulsion is obtained, but when it is associated with gum acacia, the emulsion cracks no sooner it comes out of the colloid mill. Even as high as ten per cent of gum acacia could not produce any stable emulsion. When the percentage of the bile salt is as low as 0·1, emulsification is possible.

The effect of emulsifiers of group (*ii*) such as egg-albumin and saponin, is not antagonistic against gum acacia as is apparent from what has been said above. All of them form tough films at the interface and therefore mixtures of these emulsifiers produce better emulsion.

The effect of gum tragacanth, agar agar and Irish moss in presence of gum acacia is interesting. The emulsions prepared with the three emulsifiers separately are very thick and coarsely dispersed and water separated slowly on standing. It indicates that viscosity alone is not the only criterion of stabillty of an emulsion. These emulsifiers are only thickening agents and are poorly adsorbed. Although 0·8% of tragacanth converts the emulsion to W-O, it does not antagonise with gum acacia probably for its low adsorbability. It is, however, observed that increasing additions of gum acacia along with these thickening agents produce less viscous emulsion and at a certain stage the emulsion becomes so thin that water separates rapidly. The liquefying action of neutral salts on agar jelly is well known. The same type of liquefaction is obtained by the action of gum acacia on agar agar, gum tragacanth and Irish moss.

When gum tragacanth is used with bile salts, there was no immediate cracking of emulsion as with gum acacia. By offering viscosity, gum tragacanth stabilises the bile salt emulsion for longer periods but the separation of oil at the top in the long run is not prevented.

TABLE III.

Thickening effect of gum tragacanth.

Gum traga.	Bile salt.	Remarks.
0·5%	0·05%	Cracks rapidly.
0·5	0·5	Cracks less rapidly.
0·5	1·0	Fine; oil separates very slowly.
1·0	1·0	Coarse; oil separates slowly from the beginning.
	Lecithin.	
0·5	0·1	Cracks rapidly.
0·5	0·5	Oil separates very slowly.
1·0	0·5	Oil separates slowly from the beginning.
	Egg-albumin.	
0·5	0·1	Little or no oil or water separates.
1·0	0·1	Oil separates from the beginning.
	Turkey Red.	
0·5	0·75	Oil separates slowly from the beginning.
1·0	0·75	,, rapidly ,, ,,
	Gelatin.	
0·5	0·05	Coarse, oil separates from the beginning.
0·5	0·4	Thick, Fine; no oil or water separates.
1·0	0·4	Oil separates from the beginning.
	Saponin.	
0·5	0·04	Fine, thick, no oil or water separates.
1·0	0·04	Oil separates from the beginning.

TABLE IV.

Emulsions with several other combinations.

Bile salt	1·0%	Irish Moss	1·0%	Oil and water	separate	from	beginning.
Sodium oleate	0·2	,,	1·5	,,	separate	rapidly	,,
Turkeyred oil	0·75	Agar agar	0·4	,,	,,	slowly	,,
Egg-albumin	0·1	Lecithin	0·5	Thin	,,	,,	,,

From what has been said above, the general conclusion can be drawn that emulsifiers of the group (*i*) antagonise with the other groups and cause liberation of free oil at the top. Emulsifiers of the groups (*ii*), (*iii*) and (*iv*) do not have mutual antagonistic action. If however a large amount of gum acacia is used with emulsifiers of group (*iii*), the emulsions lose consistency, become thin and water separates at the bottom quickly.

Investigations on the change of physical and chemical properties of mixtures of emulsifying agents are now in progress.

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Dyes Derived from Isatin. Azines and Indigoid Vat Dyes.

By Sisir Kumar Guha and Hariprasad Basu-Mallick.

In view of the interesting tinctorial properties of acenaphthenoacenaphthazine and its various substituted products (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 679), the present investigation was undertaken to prepare similar azines in the isatin series and to study how far they are comparable with those of the corresponding compounds in the acenaphthenequinone series.

The paper deals with the preparation and properties of azine dyes obtained by condensing 2:3-diaminoacenaphthene (Sachs and Mosebach, *Ber.*, 1911, **44**, 2852) with isatin, 5-nitro-, and its 5:7-dinitro derivatives. These azines are yellow, brownish yellow and brown. The yellow shade developed on wool from acenaphthenoindazine is in no way inferior to that of the same shade obtained from acenaphthenoacenaphthazine (*cf.* Guha, *loc. cit.*). It has also been observed that unlike acenaphthenoacenaphthazine, acenaphthenoindazine is not attended with a marked increase in the depth of the colour on introduction of nitro-groups. For the sake of convenience, a comparison of the colour of the dyeings on wool of some of these classes of compounds is given below:

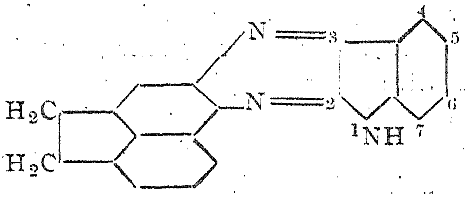
Compound.	Colour of the dyeings on wool.
Acenaphthenoindazine	Yellow
Acenaphthenoacenaphthazine	Yellow
Acenaphtheno-5:7-dinitroindazine	Orange-yellow
Acenaphtheno-3:4-dinitroacenaphthazine	Chocolate

A few 2:3-naphthathiophene-indole-indigos are already known (Schwz. P. P., 105656/1924, *Chem. Zentr.*, 1926, **IB**, 97, 1890; Dutt, *Ber.*, 1934, **67**, 1325). Three more have now been obtained from 5-iodo-, 5-bromo-7-nitro-, and 5:7-dinitroisatin by condensation with 2:3-naphthoxythiophene (Friedländer and Woreshzow, *Annalen*, 1912, **388**, 18). They resemble the indole-methylthionaphthene-indigos (*cf.* Guha and Basu-Mallick, *J. Indian Chem. Soc.*, 1934, **11**, 396) in giving rise to the soluble vats with an alkaline hydrosulphite and in uniformly developing on cotton fast shades. The violet, deep violet and blue-violet shades developed on cotton are deeper than those of the same shades obtained from chloro-, bromo-, and nitroisatin which were privately obtained for comparison from Dr. P. C. Dutta.

EXPERIMENTAL.

The azines described below were boiled with alcohol, in which they are sparingly soluble and finally crystallised.

Acenaphthenoindazine.



A solution of isatin (0·147 g.), 2:3-diaminoacenaphthene (0·184 g.), in boiling glacial acetic acid (15 c. c.) was boiled for 1 hour, when the colour of the solution turned reddish brown and the product separated in silky brownish yellow crystals. It was collected, washed and purified by a process similar to acenaphthenoacenaphthazine (Guha, *loc. cit.*). It melts above 310°. It is soluble in pyridine, moderately soluble in acetic acid and sparingly soluble in alcohol, benzene and xylene. It dissolves in strong sulphuric acid with a violet-blue colour and dyes wool in yellow shades from an acid bath. (Found: N, 14·43. $C_{20}H_{13}N_3$ requires N, 14·23 per cent).

Acenaphtheno-5-nitroindazine.—5-Nitroisatin (0·288 g.), dissolved in glacial acetic acid (35 c.c.), was mixed with a solution of 2:3-diaminoacenaphthene (0·276 g.) in acetic acid (15 c. c.). Crystalline precipitate separated from the resulting solution, which at first assumed a greenish-yellow colour quickly changing to brownish-red, the solution was boiled for half an hour and filtered hot, the precipitate washed with acetic acid and hot water. The product was crystallised from pyridine in small rectangles, subliming above 310°. It is soluble in nitrobenzene, and pyridine; sparingly soluble in acetic acid, alcohol and acetone. It gives a deep blue colouration with strong sulphuric acid and dyes wool deep yellow shades from an acid bath. (Found: N, 16·78. $C_{20}H_{12}O_2N_4$ requires N, 16·47 per cent).

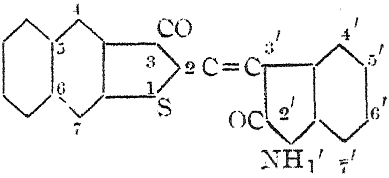
Acenaphtheno-5:7-dinitroindazine was prepared in a similar way to the preceding compound from 5:7-dinitroisatin (0·237 g.) and the diaminoacenaphthene (0·184 g.) in glacial acetic acid (60 c. c.). The brown crystalline precipitate separated from xylene in microscopic needles subliming above 310°. It is moderately soluble in acetic acid and xylene, sparingly soluble in benzene, ethyl alcohol and amyl alcohol. It dissolves in strong sulphuric acid with a deep blue coluoration and dyes wool orange-yellow shades from an acid bath. (Found: N, 18·52. $C_{20}H_{11}O_4N_5$ requires N, 18·18 per cent).

The method of procedure adopted for the preparation of the indigoid dyes described below was the same in every case.

The isatin derivative and the 2:3-naphthoxythiophene were dissolved separately in boiling glacial acetic acid and the mixed solution was treated with a few c.c. of strong hydrochloric acid and shaken, the dye was precipitated at once. The mixture was heated to boiling for 10-14 minutes, filtered hot, the precipitate washed with acetic acid and hot water and purified by boiling successively with alcohol and acetic acid and crystallised.

These indigoid dyes are soluble in pyridine, nitrobenzene and aniline; sparingly soluble in alcohol, acetone, amyl alcohol, chloroform and benzene. They melt above 395° and on further heating volatilise evolving coloured vapours. The first two of the undermentioned dyes give a green colouration with strong sulphuric acid from which water reprecipitates the original dyes and they form deep yellow vat from which the dye is developed on cotton by atmospheric oxidation.

2:3-Naphthathiophene-3'-(5'-iodo)-indole-indigo.



It was prepared from 5-iodoisatin (1·365 g.) and 2:3-naphthoxythiophene (1 g.) in 120 c. c. of glacial acetic acid and 7 c. c. of concentrated hydrochloric acid. It separated from pyridine in fibre-like red-violet needles. It is moderately soluble in acetic acid and xylene. It dyes violet shades on cotton. (Found: S, 7·42. $C_{20}H_{10}O_2NIS$ requires S, 7·03 per cent).

2:3-*Naphthathiophene*-3′-(5′-*bromo*-7′-*nitro*)-*indole-indigo* separated as deep violet crystals by reacting 5-bromo-7-nitroisatin (0·542 g.) and the naphthoxythiophene (0·4 g.) in 70 c.c. of acetic acid and 4 c.c. of concentrated hydrochloric acid. It crystallised from pyridine as fine long needles. The dye is sparingly soluble in acetic acid, difficultly soluble in xylene. It dyes deep violet shades on cotton. (Found: Br, 17·59. $C_{20}H_9O_4N_2BrS$ requires Br, 17·66 per cent).

2:3-*Naphthathiophene*-3′-(5′:7′-*dinitro*)-*indole-indigo* was obtained as dark violet crystals by the condensation of dinitroisatin (1·18 g.) and 2:3-naphthoxythiophene (1 g.) in 122 c.c. of acetic acid and 7-9 c.c. of concentrated hydrochloric acid. It crystallised from nitrobenzene in shining rectangular crystals. It dissolves in strong sulphuric acid with a bluish green colouration and dyes cotton in blue-violet shades from an orange-yellow vat. (Found: S, 7·39. $C_{20}H_9O_6N_3S$ requires S, 7·63 per cent).

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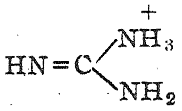
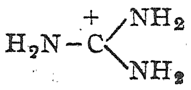
Raman Effect and Molecular Structure. Part I. The Structure of the Guanidinium Ion.

By Jagannath Gupta.

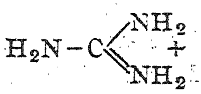
It is well known that guanidine, $HN=C(NH_2$ $_2$, inspite of its containing two amino groups, is a strong mono-acid base. The corresponding ion, therefore, has the apparent possibility of assuming any of the three following structures :



(I)



(II)



(III)

Investigations on the crystal structures of guanidinium halides have served to clear up the question only partially. Theilacker (*Z. Krist.*, 1935, **90A**, 51, 256) has shown that in the guanidinium ion, all the three nitrogen atoms are crystallographically equivalent and the ionic character can not be associated with any particular nitrogen atom. This result, therefore, cancels the probability of structure (I), although it can not decide between structure (II), and a resonance structure between the three double bonded forms of type (III).

It is evident that the problem is intimately connected with the question, whether or not an imino group can function as a basic unit in neutralisation reactions. Although the basic activity of the imino group is least expected in a molecule like guanidine, which already contains two other amino groups, the consistently mono-acidic character of the base raises this unusual possibility. It was thought that a study of the Raman effect of the ion might throw some light on the problem, and the results of the investigations are described and discussed in the present paper.

EXPERIMENTAL.

Water for preparing solutions.—Distilled water was thrice redistilled in vacuum to render it free from dust and fluorescent impurities.

Guanidine Nitrate.—The pure substance was recrystallised from distilled water containing a little nitric acid and the crystals washed several times with the redistilled water. A saturated solution (30 c. c.) was then prepared and kept over 0·5 g. of activated charcoal* (prepared from extra pure glucose) for several hours About 1 g. of extra pure crystallised potassium bromide was added †, and the solution filtered repeatedly through double folds of gravimetric filter papers. The filtrate was finally run directly into the Wood's tube, when the solution was ready for exposure.

Guanidine Hydrochloride.—Pure guanidine carbonate was gradually added to hydrochloric acid (1 : 1) kept cooled in water, keeping excess of acid. The solution, after warming on the water-bath to remove all carbon dioxide, was filtered and allowed to crystallise in a desiccator over concentrated sulphuric acid. The mother liquor was drained off from the crystals by suction and the latter washed with chemically pure concentrated hydrochloric acid. The pure crystals thus obtained were dissolved in a very small quantity of water, containing a little pure HCl to prevent hydrolysis. KBr (1 g.) was added to the solution which was then repeatedly filtered as before till free from any suspended impurities. The tubes were illuminated by the condenser method using a quartz mercury arc lamp as the source of illumination. The illumination was increased with a metal reflector. A solution (4%) of *m*-dinitrobenzene in benzene was used to cut off the 4046Å group of mercury lines, and a dilute solution of *o*-cresolphthalein in NaOH to remove the faint mercury bands to the shorter wave-length side of the 4916Å mercury line, for unequivocal detection of faint Raman lines in this region.

For the polarisation experiment, the arrangement described by the present author in a previous paper (*Indian J. Phys.*, 1936, **10**, 313) was used. The results are shown in the following table.

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* Kindly supplied by the Department of Physical Chemistry.

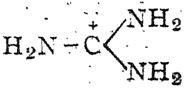
† Repeated experiments have shown that the addition of small quantities of KBr or KI effectively reduces the continuous background usually observed in the scattered spectrum of aqueous solutions. The actual part played by the salt is not clear.

Guanidine-nitrate soln.		Guanidine hydrochloride soln.		
$\Delta\nu$.	Intensity and width of lines (visual).	$\Delta\nu$.	Intensity and width of lines.	Polarisation characters.
520	1	522	1	$\rho > 0{\cdot}5$
997	3	995	4	$\rho < 0{\cdot}2$
1045	3			
1350	1 b			
1610	1 b	1620	$\frac{1}{2}$ b	$\rho > 0{\cdot}5$

DISCUSSION OF RESULTS.

As can be seen from the preceding table, the Raman lines attributable to the guanidinium ion are in the region of 520, 1000 and 1620 wave-numbers. The extra lines at 1045 and 1350 wave-numbers are associated with the vibrations of the NO_3^- ion (*cf.* Nisi, *Proc. Phys. Math. Soc. Japan*, 1933, **15**, 114). The line at 995 cm^{-1}, attributed to guanidinium ion is intense, sharp and strongly polarised.

From the theory of the origin of Raman scattering, it is well known that those vibrations, which are completely symmetrical, *i.e.*, which are not attended with any change in the electric moment of the molecule, and are "forbidden" in the infra-red absorption spectra, give rise to the most intense Raman lines of very small depolarisation factors. It can, therefore, be asserted with some confidence that the line at 995 cm^{-1} owes its origin to the totally symmetrical vibration of three NH_2-groups against the carbon atom at their centre, much like the oscillations of the oxygen atoms against the central C and N atoms in carbonates and nitrates respectively. The low value of the frequency shift, *viz.*, about 1000 wave-numbers, rules out the possibility of the double bonded resonance structure (III) and lends every support to the formula



$$H_2N-\overset{+}{C}\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} \quad (II).$$

The faint band in the region of 1620 wave-numbers goes to indicate that the ions may not all be of one form but may possess a small percentage of the form containing the double bond (III), in asmuch as the value of the shift is close to the value 1650 cm^{-1}, attributed to the C = N group, as shown in the oximes (*cf.* Bonino and Manzoni-Ansidei, *Mem. Accad. Italia*, 1933, **4**, 759: *Z. physikal. Chem.*, 1933, **22B**, 169) in dicyandiamide (*cf.* Dadieu and Kohlrausch, *Monatsh.*, 1931, **57**, 225) etc. Judging from the fact that the line at 1650 cm^{-1} which appears in compounds containing C = N grouping is usually strong, it appears from the very feeble intensity of the line at about 1620 cm^{-1} in the guanidinium ion, that the percentage of molecules containing the double bonded structure is certainly not large in the solution. The possibility of the line coming from guanidine itself which might have been formed by hydrolysis should not also be overlooked, in asmuch as the intensity of the line is less in an acid solution of the hydrochloride than in a neutral solution of the nitrate.

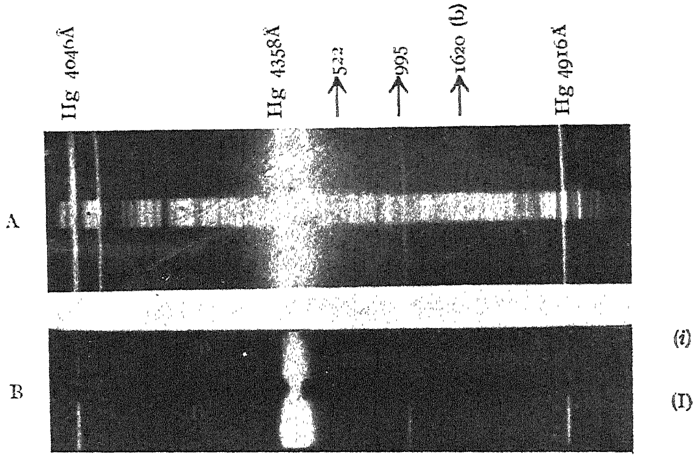
The next point of particular interest is to examine whether any information regarding the spatial distribution of the atoms can be deduced from theoretical considerations, *e.g.*, whether the C atom lies in the same plane as that containing the three N atoms, or otherwise. According to the polarisability theory of the origin of Raman lines as developed by Placzeck (Handbuch der Radiologie, Vol. VI, Leipzig, 1934) on the symmetry properties of molecules, a molecule of the type YX_3 gives rise to the following fundamental frequencies:

(*a*) When Y lies in a plane different from that containing the three X atoms (symmetry C_{3v})—two totally symmetric oscillations and two degenerate, all of which are active both in Raman scattering and infra-red absorption.

(*b*) When Y lies in the same plane as containing the three X atoms (symmetry D_{3h})—one totally symmetric oscillation, active in Raman scattering and forbidden in infra-red absorption, one antisymmetric oscillation, in Raman scattering generally forbidden, and two degenerate, symmetrical to the plane, active in Raman scattering, but usually do not give rise to so sharp and intense Raman lines as symmetric vibrations do.

In the Raman spectra of a molecule of the type (*b*), therefore, there are expected three lines, one strong and highly polarised, due to the totally symmetric oscillation, and two less intense lines, completely depolarised, *i.e.*, having $\rho = 6/7$.

The experimental results show only one strongly polarised Raman line and not two. On the basis of Placzeck's theoretical considerations,



A. Raman spectra of guanidine hydrochloride in water.

B. Polarisation of the 995 line.

(*i*) Weak component.

(I) Strong component.

it can therefore be definitely stated that the guanidinium ion possesses a planar structure.

The ion, therefore, completely resembles the nitrate or the carbonate ion, where three similar atoms are at the three corners of an equilateral triangle and the central N or the C atom is at the intersection of the medians. This is in complete agreement with the conclusions arrived at by Theilacker from X'ray analysis and investigations of the optical properties of crystals of guanidinium iodide (*Z. Krist.*, 1935, **90A**, 51, 77).

In conclusion, the author wishes to express his respectful thanks to Sir P. C. Rây for his kind interest in the work, and to Prof. D. M. Bose for his kindly permitting the author to work in the Palit Laboratory of Physics. The work was carried out under kind supervision of Dr. S. C. Sirkar, to whom also the author's best thanks are due.

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Studies on the Addition of Hydrogen Halides to Butadiene.

By S. N. Ganguly.

If it is held that the butadienoid unit may polarise in two ways

$$(i)\ \overset{+}{C}_1-\overset{-}{C}_2-\overset{+}{C}_3-\overset{-}{C}_4, \quad \text{and} \quad (ii)\ \overset{-}{C}_1-\overset{+}{C}_2-\overset{-}{C}_3-\overset{+}{C}_4,$$

leading to reaction at adjacent C atoms of the chain, it can be expected that the addition of a substance of the nature $\overset{+}{A}-\overset{-}{B}$ to butadiene should yield 3 isomerides of the types (1) $CH_2A-CHB-CH=CH_2$, (2) $CH_2A-CH=CH-CH_2B$ and (3) $CH_2B-CHA-CH=CH_2$ depending upon whether the addition takes place at 1:2, 1:4 or 3:4 carbon atoms of the chain.

Addition of bromine to butadiene was studied by Grinner (*Compt. rend.*, 1863, **116**, 723 ; 1864, **117**, 553) and of chlorine by Muskat and Northup (*J. Amer. Chem. Soc.*, 1930, **52**, 4043). In both these cases, the authors obtained both 1:2- and 1:4- isomerides, only two being theoretically possible.

Addition of ICl to the hydrocarbon was examined by Ingold and Smith (*J. Chem. Soc.*, 1931, 2754) and they could trace the presence of only two isomerides namely (1) $CH_2I-CHCl-CH=CH_2$ and (2) $CH_2I-CH=CH-CH_2Cl$, whereas the third theoretically possible isomeride, (3) $CH_2Cl-CHI-CH=CH_2$ was never obtained.

Since the entrance of the iodine atom is regarded as marking the point of incidence of the reaction, this experiment fovours the view that the point of incidence of the reaction in the butadienoid chain is C_1 and not the C_2 atom.

In the addition of hydrogen halides, however, the point of incidence of the reaction, as deduced from the polarity of the substituents, is marked by the point of entrance of hydrogen. The stable position of the halogen then depends on anionotropic equilibrium as affected by the substituents present, including that which has become modified by the accession of the hydrogen atom. The first of these conclusions is confirmed, without complications related to the second, by the formation of compounds having the properties of allyl halide, from *cyclo*pentadiene and *cyclo*hexadiene, The hydrogen of the hydrogen halide attaches to the C_1 atom (Kraemar and Spilker, *Ber.*, 1896, **29**, 554; Crossly, *J. Chem. Soc.*, 1904, **85**, 1420).

In support of the second view, already mentioned, reference may be made to Farmer and Marshall's demonstration that the monohydrobromide of dimethylbutadiene [$CH_2{:}C(Me){\cdot}C(Me){:}CH_2$] prepared under a variety of conditions, in all cases consist essentially of the product [$H{\cdot}CH_2C{\cdot}(Me){:}C(Me){\cdot}CH_2Br$] (*J. Chem. Soc.*, 1931, 139).

In the light of these results it can be expected that the addition of HBr or HCl to butadiene should yield only two isomerides, namely (1) $CH_3{\cdot}CHX{\cdot}CH : CH_2$ and (2) $CH_3{\cdot}CH : CH{\cdot}CH_2X$; the possibility of the formation of the third one, $CH_2X{\cdot}CH_2{\cdot}CH{:}CH_2$ being thus ruled out on theoretical grounds.

Addition of hydrogen chloride to the hydrocarbon resulted in the formation of two addition products which were identified as $\Delta^{3:4}$-2 chlorobutene and $\Delta^{2:3}$-4 chlorobutene.

To effect a direct comparison of these addition products with authentic specimens, the two chlorobutenes were prepared from methylvinyl carbinol by treatment with four or five times its weight of concentrated hydrochloric acid.

An attempt has been made to prepare the hitherto-undescribed isomeric chlorobutene ($CH_2Cl{\cdot}CH_2{\cdot}CH{:}CH_2$) from allyl carbinol, prepared by the action of *para*-formaldehyde on allyl bromide in presence of magnesium (Pariselle, *Ann chim.*, 1928, **9**, 412). On treatment with concentrated hydrochloric acid, the compound obtained was mostly a di-addition product instead of the desired chlorobutene.

Since no definite conclusion could be reached as to the absence of the third isomeride, namely $CH_2Cl{\cdot}CH_2{\cdot}CH{:}CH_2$, no attempt was made to determine quantitatively the proportion of the $\triangle^{3:4}$-2- and $\triangle^{2:3}$-4- chlorobutenes in the reaction product. Such a determination of the percentage composition of the mixture was proposed to be accomplished from the refractive index composition curve, which according to expectations was found to be a straight line.

Addition of hydrogen bromide resulted in the formation of only one compound, b.p. 104-107°, identified to be $CH_3{\cdot}CH : CH{\cdot}CH_2Br$ by comparing its properties with an authentic specimen of the same, prepared synthetically from methylvinyl carbinol.

Transformation of the crude addition product to the acetoxy derivative was also tried. On purification and final distillation, a product boiling at 130-35° was collected. This was identified to be $CH_3\cdot CH:CH\cdot CH\cdot O\cdot COCH_3$ by direct comparison with an authentic specimen of the same.

On an attempt to study the action of hydrogen bromide on methylvinyl carbinol Baudrengheim (*Bull. Soc. chim. Belg.*, 1922, **31**, 160) obtained only one substance namely $\Delta^{2:3}$-4-bromobutene, whereas the isomeride $\Delta^{3:4}$-2-bromobutene which was more likely to be formed by the reaction, could not be isolated from the reaction product. This suggests, however, that $\Delta^{3:4}$-2-bromobutene, which might have been formed at the start, subsequently underwent anionotropic change in a similar manner as observed by Farmer ond Marshall in the preparation of monohydrobromide of dimethylbutadiene to the more stable variety.

The above argument regarding the anionotropic change of the $\Delta^{3:4}$-2- to $\Delta^{2:3}$-4-bromobutene, gains more support in view of the fact that while both the corresponding acetoxy derivatives are known to be perfectly stable compounds, bromobutene has not yet been successfully isolated by any method.

The difference between the behaviour of hydrogen chloride and hydrogen bromide on butadiene is probably due to the difference in their (*i*) dipole moment and thereby the permanent inductive electronic drift and more so (*ii*) the molecular volume—it being an established fact that there is a connection between the bulk of the new entrant and its orienting power (*cf.* Le Fevre, *J. Chem. Soc.*, 1933, 980 ; also Ganguly and Le Fevre, *ibid.*, 1934, 848, 852, 1697).

Furthermore, such an explanation is in perfect agreement to the observation of Gillet (*cf.* Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 1928, 729), who concludes that hydrogen bromide suggests itself as a probable accelerator of 1:2 → 1:4 change.

EXPERIMENTAL.

Butadiene. (*cf.* Farmer, Lawrence and Thorpe, *loc. cit.*). The gas obtained by heating "railway hydrocarbon" was passed through wash-bottles containing bromine and immersed in ice, till the latter was completely consumed. Butadiene tetrabromide, thus prepared along with other impurities was washed with ligroin and recrystallised from the same solvent till it melted at 117°.

Reduction of the Tetrabromide.—The tetrabromide thus prepared was reduced to butadiene by the method described by Thiele.

Before being collected in tubes immersed in a freezing mixture of solid carbon dioxide and ether, the gas was further purified by passing through (*i*) a spiral immersed in ice and salt; (*ii*) a calcium chloride tube immersed in a freezing mixture of ice and salt, and finally (*iii*) through phosphorus pentoxide to effect complete drying. Butadiene was collected in sealed tubes and kept in a refrigerator till further use.

The hydrogen chloride and hydrogen bromide used have been purified by passing through (*i*) moist red phosphorus, (*ii*) U-tubes containing calcium chloride and immersed in a mixture of solid carbon dioxide and ether and finally through, (*iii*) phosphorous pentoxide. The gases were then collected in Carius tubes immersed in liquid air.

Methylvinyl Carbinol.—Methyl bromide (100 g.) mixed with four or five times its volume of dry ether was added drop by drop in about an hour and a half to magnesium (24 g.), suspended in dry ether (1000 c.c.) in a three-necked round bottomed flask fitted with a reflux condenser and a mechanical stirrer. Stirring was continued during the whole operation and the temperature was kept below 15°. It was then allowed to stand for another couple of hours. Acrolein (67 g.), mixed with four or five times its volume of dry ether, was then added (with stirring) to the mixture during 2 hours. The process being complete, the flask was heated up to 15° and allowed to stand for 18 hours. The reaction product was then hydrolysed by means of a saturated solution of ammonium chloride (1000 c. c.) and just sufficient amount of hydrochloric acid. The ethereal layer was separated, dried over potassium carbonate and then barium oxide for 3 or 4 days, ether removed and the product collected at 96-97°, yield 20 g.

Addition of Hydrogen Bromide to Butadiene.—Anhydrous hydrogen bromide was added to butadiene in the proportion of 1 : 1; addition took place easily. The crude product obtained was washed with water and dried over potassium carbonate. The greater portion distilled at 101°-107° and some above 150°, with decomposition. The fraction below 101° was redistilled, but no indication of its containing a substance boiling at a definite temperature lower than 104° was obtained. The portion boiling at 101-107° was redistilled and collected at 104-107°; n_D^{20}, 1·4797; d^{21}, 1·3342.

Treatment of Methylvinyl Carbinol with Hydrobromic Acid.—Methylvinyl carbinol (20 g.) was mixed with hydrobromic acid (*d* 1·7, 50 g.) and left in a mechanical shaker for 4—5 hours. At the end of the process, the product was neutralised with potassium carbonate, washed with water and the oily layer dried over potassium carbonate and distilled at 101°-107°. It was redistilled at 101°-104° ; d^{19} 1·339 ; n_D^{20}, 1·47816.

Acetoxy Derivative of $\triangle^{2:3}$*-4-Bromobutene.*—The bromobutene was treated with fused potassium acetate, acetic acid and a trace of potassium iodide. The oily layer was dried over calcium chloride and distilled at 132°-35° ; d^{21}, 0·8539 ; $n_D^{20°}$, 1·43256.

Addition of Hydrogen Chloride to Butadiene.—The reaction was not complete even in 10 days. The crude addition product was washed with water, dried over calcium chloride and fractionated into 2 parts, (*i*) one distilling at 62°-74° and (*ii*) the other at 74°-84°. By repeating the distillation of (*i*) a substance distilling at 64·68° and (*ii*) the other at 80°, were obtained.

According to Baudrengheim (*loc cit.*) 1:2-chlorobutene ($CH_3 \cdot CH_2Cl \cdot CH:CH_2$) boils at 64-65°, whereas the corresponding 1:4-product boils at 84 85°/766 mm.

Treatment of Methylvinyl Carbinol with Hydrochloric Acid.—Methyl vinyl carbinol (20 g.) was mixed in a strong bottle with hydrochloric acid (*d* 1·16. 60 c. c.). The mixture was then left in a mechanical shaker (3 to 4 hours). The reaction mixture was then washed with water and extracted with ether. The ethereal solution was washed with sodium carbonate and again with water and the ether removed and dried over calcium chloride and distilled at 60°-87° On redistillation two fractions were obtained *viz.*, (*i*) 1:2-chlorobutene, 64°-68° /757 mm. and (*ii*) 1:4-chlorobutene, 80°/757 mm.

Refractive Index of 1 : 2-*and* 1:4-*Chlorobutenes at* 21°.

All observations on the determinations of refractive indices were done with a Pulfrich refractometer with reference to sodium D line.

Chlorobutenes		Angle of refraction.
1 :2—	1 :4—	
0 %	100 %	50° 10
21	79	52° 44
51·7	48·3	53° 59
100	0	55° 44

Acetoxy Derivative of the Addition product of Hydrogen Bromide to Butadiene.—The crude addition product was mixed with fused potassium iodide (*cf. Bull. Soc. chim. Belg.*, 1922, **31**, 160), when the mixture became almost solid, with evolution of heat. On heating it on the water-bath, the solid diminished and liquid increased. The mass was poured into water, and the acetic acid was neutralised with sodium carbonate. The oily layer was separated, dried over calcium chloride, and distilled at 130°-136°. The fraction below 130° gave the substance boiling at 130°-36° on repeated distillation, and there was no indication of its containing a definite substance with lower boiling point, and although it contained some unchanged bromo compound, no trace of $CH_3 \cdot CH(OCOCH_3) \cdot CH : CH_2$, could be isolated, d^{20}, 0·8541; n_D^{20}, 1·4.

SUMMARY.

1. Addition of hydrogen bromide to butadiene leads to the production of $\Delta^{2:3}$-4-bromobutene only.

2 Addition of hydrogen chloride to butadiene leads to the formation of two isomerides (*a*) $\Delta^{2:3}$-4-chlorobutene and (*b*) $\Delta^{3:4}$-2-chlorobutene.

3. The properties of these addition products are compared with authentic specimens of the same prepared synthetically.

4. An explanation has been advanced to interpret the results obtained in the light of the modern concepts of the electronic theory of valency.

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The Constitution of Ayapanin.

By Prafulla Kumar Bose and Anil Chandra Roy.

The leaves of *Eupatorium ayapana*, Vent. have been used in various parts of the world as a stimulant, tonic and diaphoretic. Dymock, Hooper and Warden (*Pharmacographia Indica*, Vol. II, p. 245) however remark: "The exaggerated ideas of its virtues formerly entertained are now exploded." In India the leaves or their infusion is still prescribed as an hæmostat. Dymock *et al* (*loc. cit.*) noticed the presence of an essential oil and a neutral crystalline substance, called ayapanin by them, which sublimed at 159-60° and imparted to concentrated sulphuric acid a faint yellow colour.

Recently Nag and Bose (*Trans. Bose Res. Inst.*, 1932-33, **8**, 195) described the isolation, from the dried leaves of the plant, of a white crystalline substance, m.p. 110-12°, which was also called ayapanin. According to these authors ayapanin has the molecular formula, $C_{12}H_{10}O_4$. It dissolves in concentrated sulphuric acid with a violet *colour* and in potassium hydroxide with an yellow colour. Evidently Nag and Bose's ayapanin is different from that of Dymock *et al.* Bose and Nag (*Science and Culture*, 1936, **2**, 163) have further desdescribed dibromoayapanin, $C_{12}H_8O_4Br_2$ and nitro-ayapanin, $C_{12}H_9O_4{\cdot}NO_2$.

From the fresh leaves of *E. ayapana* we have been able to isolate a crystalline product in an yield of 0·1%, *i.e.*, 0·5% calculated on the dried material. From this product, which is a mixture, we have isolated a colourless substance, crystallising in plates and having m.p. 114-15°. This substance dissolved in aqueous potassium hydroxide with an yellow colour and in concentrated sulphuric acid with a deep violet *fluorescence*. Our compound is evidently identical with the ayapanin of Nag and Bose but in a purer form. Ayapanin has a faint coumarin-like odour especially when hot and was found to contain 17·2% methoxyl. The properties of our ayapanin are in good agreement with those of herniarin (7-methoxycoumarin) isolated from *Herniaria hirsuta*, Linn. (Barth and Herzig, *Monatsh.*, 1889, **10**, 161). We have actually established the identity of our ayapanin with a synthetic specimen of 7-methoxycoumarin, which has previously been found in the flowers of *Matricaria chamomilla*, Linn. (Power and Browning, *J. Chem. Soc.*, 1914, **105**, 2284) and in lavender oil (Ellmer, *Riechstoffind.*, 1927, p. 206).

Besides ayapanin, two other substances, m.p. 220-21° (which we shall call "ayapin") and m.p. 109° respectively, have been isolated from the same source. The constitution of these compounds will form the subject of a future communication. An account of the hæmostatic properties of ayapanin and ayapin will be published elsewhere.

EXPERIMENTAL.

Isolation of Ayapanin.—Fresh leaves of *E. ayapana* were boiled with eight times the weight of water for about 3 hours and filtered hot. The extraction was repeated twice, The combined filtrates, which showed a violet fluorescence somewhat masked by the light brown colour of the solution, were cooled and thoroughly extracted with chloroform. The chloroform extracts were dried over sodium chloride, and the solvent removed on the water-bath. The greenish brown crystalline residue was sublimed in vacuum (0·2 mm). A small quantity of a reddish oil which came over below 100° was rejected and the crystalline sublimate which passed over at 100-180° was collected; yield 0·1%. The sublimate was extracted with chloroform which dissolved all the ayapanin and a little of ayapin. The chloroform extract was evaporated to dryness and the residue distilled in vacuum, the fraction boiling at 130-140°/0·2 mm. being collected. The distillate was repeatedly fractionated and the fraction boiling at 120-25°/0·2 mm. was finally collected and twice recrystallised from hot water, when colourless plates, m.p. 114-15°, of ayapanin were obtained. (Found : OMe, 17·2. Calc. for $C_{10}H_8O_3$: OMe, 17·6 per cent).

7-Methoxycoumarin melted at 114-15° and there was no depression in m.p. on being mixed with ayapanin. They showed identical crystalline form under the microscope and their behaviour towards concentrated sulphuric acid and potassium hydroxide was also identical. The identity of ayapanin with 7-methoxycoumarin is thus firmly established.

We offer our best thanks to Sir P. C. Rây for the facilities given to one of us (A. C. R.) in carrying out this investigation.

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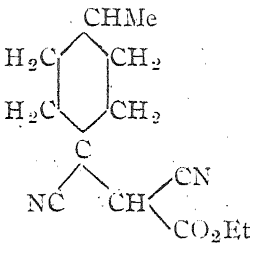
Spiro-compounds. Part II. Ring Transformation in Spiro-compound from 4-Methyl*cyclo*hexanone. A New Synthesis of Cadalene.

By Nripendra Nath Chatterjee.

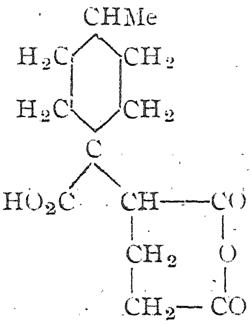
As it has not been possible to isolate the isomers demanded by Sachse's hypothesis (*Ber.*, 1890, **23**, 1323) of two strainless forms of *cyclo*hexane nor their monosubstituted or disubstituted derivatives (Werner and Conrad, *Ber.*, 1899, **32**, 3046 ; Wightman, *J. Chem. Soc.*, 1926, 2541 ; Goldschmidt and Grafinger, *Ber.*, 1935, **68**, 279 ; Dey and Linstead, *J. Chem. Soc.*, 1935, 1063 ; Desai, Hunter, Khan and Sahariya, *ibid.*, 1936, 416) the postulate of Mohr (*J. pr. Chem.*, 1918, **98**, 318) that they are easily inter-convertable holds good. Thinking that the spiro-compounds from methyl*cyclo*hexanone may differ from their *cyclo*hexanone analogoues, their study has been taken up. Such difference in behaviour has actually been observed by Birch and Thorpe (*J. Chem. Soc.*, 1922, **121**, 1821) and Desai (*ibid.*, 1932, 1049).

Freshly distilled 4-methyl*cyclo*hexanone cyanohydrin is allowed to react with the sodium salt of ethyl cyanoacetate and the sodium salt of ethyl 1-cyano-4-methyl*cyclo*hexane-1-cyanoacetate (I), thus obtained, is allowed to react with ethyl β-chloropropionate to yield diethyl 1-cyano-4-methyl*cyclo*hexane-1-α-cyanoglutarate. On hydrolysis, the above ester yields an acid anhydride (II) (corresponding ester is obtained on esterification) from which the required 1-carboxy-4-methyl*cyclo*hexane-1-α-glutaric acid is obtained after treatment with alkali. Triethyl 4-methyl*cyclo*hexane-1-carboxylate-1-α-glutarate (III), obtained by esterifying the above acid, when subjected to the action of sodium in benzene yields diethyl 4-methyl*cyclo*hexane-spiro*cyclo*pentane-2′-one-3′ : 5′-dicarboxylate (IV). It is hydrolysed by means of dilute sulphuric acid (20%) to yield 4-methyl*cylclo*hexane-spiro*cyclo*pentane-2′-one-5′-carboxylic acid. The ester (V) of the above keto-acid is subjected to the action of methyl magnesium iodide when compound (VI) is obtained. It is observed that during dehydrogenation of the spiro-compound (VI) cadalene (VII) is obtained.

A large number of sesquiterpenes are stated to have naphthalene ring structure, the experimental basis for this being the fact that on sulphur or selenium dehydrogenation they give rise to cadalene or eudalene. But this conclusion is essentially based on the fact that whatever be the nature of ring structure that is initially present in them, it is not altered during this reaction. In view of certain observations described above, this conclusion is, however, not justifiable, though not impossible.

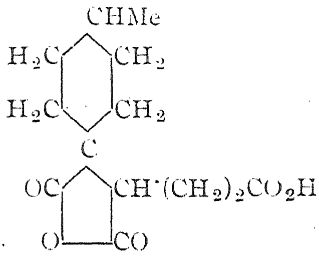


(I)



(II)

or



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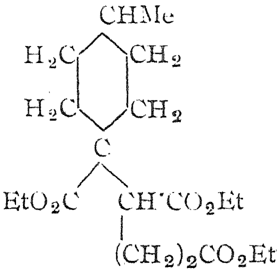

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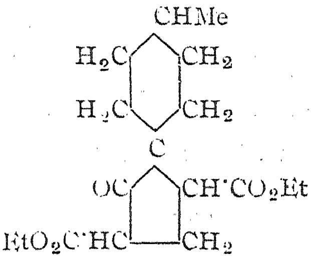

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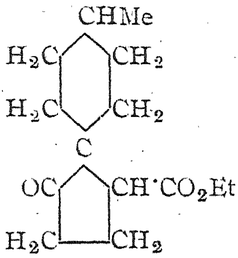

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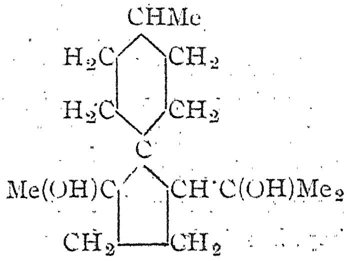

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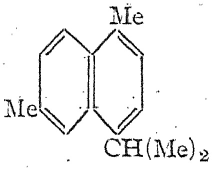

(VII)

The spiro-compound (IV) obtained is found to differ in no way from *cyclo*hexane analogue with respect to its formation (Chatterjee, *J. Indian Chem. Soc.*, 1936, **13**, 536). As no suitable reagent could be found which preferentially attacks the one, leaving the other intact, nothing definite can be said at present as regards the difference in their stability, or in other words they may be said to have got equal stability.

From the consideration of the multiplaner structure of *cyclo*hexane ring two or more isomers of the acids obtained are possible and work is in progress to separate them.

EXPERIMENTAL.

*Diethyl 1-Cyano-4-methyl*cyclo*hexane-1-cyanoglutarate.*—To a well cooled solution of freshly distilled 4-methyl*cyclo*hexane cyanohydrin (190 g.) in absolute alcohol (190 c.c.), a suspension of ethyl sodiocyanoacetate, obtained from ethyl cyanoacetate (168 g.), sodium (33 g.) and alcohol (500 c. c.), was gradually added with vigorous shaking. The mixture after being kept in ice for 6 hours and at room temperature for 3 days, was mixed with ethyl β-chloropropionate (125 g.) and after initial reaction had abated, boiled under reflux until a test portion, diluted with water was neutral to litmus (about 40 hours). The mixture was filtered and the filtrate diluted with water and extracted with ether; the ethereal extract was washed with a large volume of water to remove most of the alcohol, dried and ether recovered. It distilled as a viscous liquid, b.p. 208°-215°/4 mm., yield 150 g. (Found: C, 64·5; H, 7·7. $C_{18}H_{26}O_4N_2$ requires C, 64·6; H, 7·7 per cent).

*1-Carboxy-4-methyl*cyclo*hexane-1-α-glutaric Acid.*—The ester (20 g.) was mixed with 6 vols. of 70 % sulphuric acid and boiled under reflux for 12 hours. The condenser was removed from the flask from time to time to allow the alcohol formed to escape. The solution was then diluted with water and extracted with ether and the acid thus obtained, was freed from neutral matter by extraction with sodium carbonate. The resulting product (an acid anhydride) was heated on a water-bath with a solution of caustic alkali (15 %) for 3 to 4 hours. It was then acidified and extracted with ether. After removing ether, the product was kept in a desiccator when it solidified. It crystallised from dilute hydrochloric acid, m.p. 155°, yield

10 g. (Found: C, 57·4; H, 7·4. $C_{13}H_{20}O_6$ requires C, 57·3; H, 7·3 per cent).

The crude acid anhydride was esterified by passing alcohol vapour through a mixture of it in alcohol containing sulphuric acid. The product obtained after working up in the usual manner was found to distill in vacuum, but solidified on attaining the room temperature. It was crystallised from ether, m.p. 79°. (Found: C, 63·7; H, 8·1. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·8 per cent).

*Triethyl 4-Methyl*cyclo*hexane-1-carboxylate-1-α-glutarate* was obtained from the acid by the alcohol vapour method. The acid (59 g.), absolute alcohol (159 g.), concentrated sulphuric acid (14 c.c.), 6 litres of alcohol vaporised (7 hours) gave 60 g. of the ester, b p. 175°-180/5 mm. (Found: C, 64·1; H, 8·9 $C_{19}H_{32}O_6$ requires C, 64·04; H, 8·9 per cent).

*Diethyl 4-Methyl*cyclo*hexane-spiro-*cyclo*pentane-2′-one-3′:5′-dicarboxylate.*—A mixture of the foregoing ester (20 g.) and granulated sodium (2·3 g.) in dry benzene (50 c.c.) was refluxed for 10 minutes to start the reaction. The heating was discontinued until the vigour of the reaction abated and was then continued for 2 hours. After cooling, the product was treated with cold dilute sulphuric acid and the benzene layer was washed with aqueous sodium carbonate and with water, dried and evaporated. The residue in alcoholic solution gave a violet colouration with ferric chloride. The ester was obtained as a pale yellow oil (8 g.), b.p. 180°-185°/4 mm. (Found: C, 65·7; H, 8·1. $C_{17}H_{26}O_5$ requires C, 65·8; H, 8·3 per cent).

*4-Methyl*cyclo*hexane-spiro-*cyclo*pentane-2′-one-5′-carboxylic Acid.*—The ester was refluxed with excess of dilute sulphuric acid (20 %) for 12 hours and the cooled solution saturated with ammonium sulphate and repeatedly extracted with ether, the extract washed with water and dried with anhydrous sodium sulphate. After removing the ether it was kept in a desiccator when it crystallised as needles, m.p. 130° (after previous softening). (Found: C, 68·3; H, 8·5. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·5 per cent).

The *semicarbazone*, crystallised from absolute alcohol, m.p. 228°. (Found: N, 15·3. $C_{13}H_{21}O_3N_3$ requires N, 15·7 per cent).

*Ethyl 4-Methyl*cyclo*hexane-spiro-*cyclo*pentane-2′-one 5′-carboxylate.*—The ester prepared by refluxing a solution of the keto-acid (10 g.) in absolute alcohol (40 c.c.) with the addition of absolute alcohol (5 c.c.) saturated at 0° with hydrogen chloride, formed a colourless viscous oil (10 g.), b.p. 133°/4 mm. (Found: C, 70·5; H, 9·2. $C_{14}H_{22}O_3$ requires C, 70·5; H, 9·2 per cent).

*Action of methyl magnesium iodide on Ethyl 4-Methyl*cyclo*hexane-spiro*-cyclo*pentane-2′-one 5′-carboxylate.*—The ester (10 g.) diluted with dry ether (10 c.c.) was slowly added to a solution of methyl magnesium iodide (prepared from 3·6 g. of magnesium, 100 c. c. dry ether and 11 c.c. of methyl iodide) cooled in ice-water. After standing for 12 hours at the ordinaty temperature, the product was decomposed with ice and dilute hydrochloric acid. The solution was extracted several times with ether and the extract was washed with water, dried and evaporated. The brown residue was boiled with a solution of potassium hydroxide (10 g.) in water (10 c.c.) and alcohol (90 c.c.) for 1 hour, the alcohol removed and the residue diluted with water and repeatedly extracted with ether. (The alkaline solution was acidified with hydrochloric acid and again extracted with ether when an acid is obtained.) On removing ether a neutral oil was obtained. This oil (5 g.) and selenium (30 g.) were heated at 290°-300° for 20 hours. The temperature was then raised to 330° and kept there for 30 hours. The product of reaction was extracted with ether and the ethereal extract washed several times with water and dilute alkali. On removing ether an oil was left which was converted into picrate. It was identified as cadalene picrate, m.p. 115° alone or mixed with an authentic sample of cadalene picrate.

*Oxidation of 4-Methyl*cyclo*hexane-spiro*-cyclo*pentane-2′-one-5′-carboxylic Acid.*—The keto-acid was warmed with an excess of concentrated nitric acid until most of the red fumes had been evolved. The resulting solution was then boiled for a few minutes, and finally evaporated to dryness. The residue was treated with water and again evaporated. The semi-solid mass thus obtained was heated when carbon dioxide escaped with the formation of hexahydro-*p*-toluic acid. It crystallised from formic acid, m.p., 111° (*lit.* 111°.)

Sincere thanks of the author are due to Professor Dr. P. C. Mitter for encouragement and advice during the course of this work and thanks are also due to Mr. N. Guha for semi-micro analysis.

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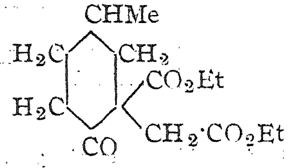
Synthesis of Diphenyl Acetates.

By Nripendra Nath Chatterjee.

The present investigation describes the synthesis of diphenyl acetates which are intermediates in the synthesis of phenanthrenes according to the method previously described by the author (*J. Indian Chem. Soc.*, 1935, **12**, 591).

4-Methyl*cyclo*hexanone-2-carboxylic ester, obtained by the method of Kötz and Michels (*Annalen*, 1906, **348**, 95), is condensed with ethyl chloroacetate when diethyl 4-methyl*cyclo*hexanone-2-carboxylate-2-acetate (I) is obtained. This on hydrolysis yields 4-methyl*cyclo*hexanone-2-acetic acid (II). After esterfication it is treated with phenyl magnesium bromide when ethyl 1-hydroxy-4-methylhexahydrodiphenyl-2-acetate (III, R = Me) is obtained. This on dehydrogenation by means of sulphur yields ethyl 4-methyldiphenyl-2-acetate (IV) (*cf.* Sherwood, Short and Woodcock, *J. Chem. Soc.*, 1936, 322).



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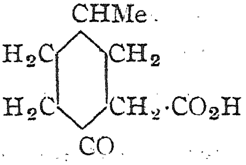

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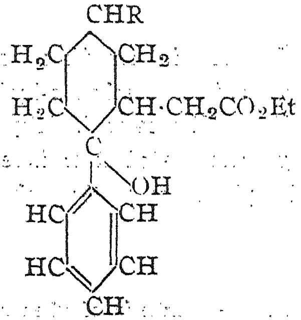

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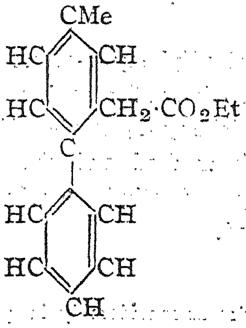

(IV)

By following the same method, 6-methyldiphenyl-2-acetate has been prepared from 6-methyl*cyclo*hexanone-2-carboxylic ester (Kötz, *Annalen*, 1905, **342**, 321).

In the preparation of diethyl 5-methyl*cyclo*hexanone-2-carboxylate-2-acetate by Kötz and Bieber's method (*Annalen*, 1906, **350**, 240) for the synthesis of ethyl 5-methyldiphenyl-2-acetate, it is observed that the product of reaction of 5-methyl*cyclo*hexanone-2-carboxylic ester and ethyl chloroacetate is always contaminated with 2-methylhexane-1: 5:6- tricarboxylic ester, formed by the ring fission. The boiling point of the above product recorded by us when the reaction is carried out in benzene in presence of molecular sodium is 163°-166°/5 mm. Further we notice the following difference between Kötz's and our compound.

Kötz.	The present author.
B.p. 194°-195°/12 mm.	B.p. 163°-66°/5 mm.
↓ On hydrolysis with methyl alcoholic potash	↓ On hydrolysis with conc. HCl
5-Methyl*cyclo*hexanone-2-acetic acid (gummy)	5-Methyl*cyclo*hexanone-2-acetic acid (crystalline, m.p. 94-95°
↓ Esterified either through Ag salt or by HCl method	↓ Esterified by HCl method
Very poor yield of ethyl 5-methyl*cyclo*hexanone-2-acetate (b. p. not definite due to poor yield), semicarbazone, m.p. 116°.	Good yield of ethyl 5-methyl*cyclo*hexanone-2-acetate (b.p. 137°/5 mm) semicarbazone, m.p. 174-75°.

Hexahydrodiphenyl-2-acetic acid* (V), an intermediate for the synthesis of phenanthrene, has been prepared from ethyl 1-hydroxyhexahydrodiphenyl-2-acetate (III, R=H). The ester is dehydrated by Darzen's method and the resulting unsaturated ester is reduced catalytically and ethyl hexahydrodiphenyl-2-acetate, thus obtained, is hydrolysed.

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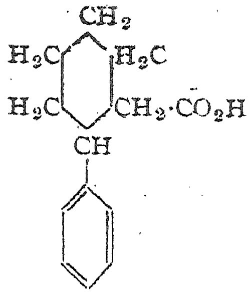
* The work was considerably in progress for the synthesis of phenanthrene from hexahydrodiphenyl-2-acetic acid when the result of Cook, Hewett, and Lawrence was published (*J. Chem. Soc.*, 1936, 71).



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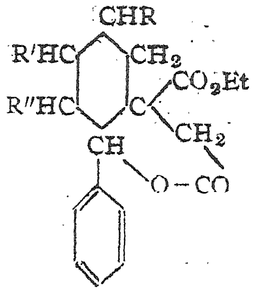

(VI)

Diethyl 4 (5 or 6)-methyl*cyclo*hexanone-2-carboxylate-2-acetate when submitted to Grignard's reaction with phenyl magnesium bromide gives latones (VI, R = Me, R′ = R″ = H; R′ = Me, R = R″ = H; R″ = Me; R = R′ = H).

Further work in this line is in progress.

EXPERIMENTAL.

*Diethyl 4-Methyl*cyclo*hexanone-2-carboxylate-2-acetate.*—Ethyl 4-methyl*cyclo*hexanone-2-carboxylate (20 g.) was added to a solution of sodium (2·5 g.) in alcohol (25 g.) and the solid sodium salt obtained was heated under reflux for 6 hours with ethyl chloroacetate (15 g.). After dilution the product was extracted with ether, and distilled at 165°/5 mm., yield 14 g.

Substitution of molecular sodium in benzene for sodium ethoxide gave a very good yield. 2·5G. of molecular sodium in 100 c.c. of benzene were added to 20 g. of ethyl 4-methyl*cyclo*hexanone-2-carboxylate and left overnight; the solid sodium salt was then heated under reflux for 3–4 hours with ethyl chloroacetate (15 g.). The product was worked up in the usual manner, b. p. 165°/5 mm., yield 20 g. (Found: C, 62·0; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1 per cent).

The *semicarbazone* crystallised from ethyl alcohol, m. p. 174°. (Found: N, 12·6. $C_{15}H_{25}O_5N_3$ requires N, 12·8 per cent).

*Diethyl 5-Methyl*cyclo*hexanone-2-carboxylate-2-acetate,* obtained from 5-methyl*cyclo*hexanone-2-carboxylate and ethyl chloroacetate by the previously described method, distilled at 163°-66°/5 mm. (Found: C, 62·1; H, 8·0. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·1 per cent).

*Diethyl 6-Methyl*cyclo*hexanone-2-carboxylate-2-acetate,* obtained from 6-methyl*cyclo*hexanone-2-carboxylic ester and ethyl chloroacetate, distilled at 158°-162°/8 mm. (Found : C, 62·0 ; H, 8·0. $C_{14}H_{22}O_5$ requires C, 62·25 ; H, 8·1 per cent).

4-*Methyl*cyclo*hexanone-2-acetic Acid.*—Diethyl *cyclo*hexanone-2-carboxylate-2-acetate (20 g.) was boiled with 2 vols. of HCl (*d* 1·19) and water (2 : 8) for 8 hours on a sand-bath. After removal of the HCl under reduced pressure, 4-methyl*cyclo*hexanone-2-acetic acid distilled at 160-165°/6 mm., yield 10 g. (Found : C, 63·4 ; H, 8·2. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent).

5-*Methylhexanone-2-acetic Acid* was obtained from diethyl 5-methyl-*cyclo*hexanone-2-carboxylate-2-acetate (20 g.). After removal of the mineral acid under reduced pressure it distilled at 162° /4 mm. and solidified at the room temperature. It crystallised from petroleum ether, m. p. 94-95° ; yield 8-10 g. (Found : C, 63·5 ; 8·1. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent).

6-*Methyl*cyclo*hexanone-2-acetic Acid*, obtained from diethyl 6-methyl*cyclo*hexanone-2-carboxylate-2-acetate, distilled at 162-166°/6 mm. (Found: C, 63·4 ; H, 8·0. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent).

Ethyl 4-*Methyl*cyclo*hexanone-2-acetate.*—4-Methyl*cyclo*hexanone-2-acetic acid (10 g.) was esterified at room temperature with 3 parts of alcohol, saturated at 0° with dry hydrochloric acid and keeping overnight. After dilution it was extracted with ether and worked up in the usual manner, b p. 129°, 8 mm., yield 8 g. (Found : C, 66·5 ; H, 9·0. $C_{11}H_{18}O_3$ requires C, 66·6 ; H, 9·0 per cent).

The *semicarbazone* crystallised from alcohol, m. p. 210-11°. (Found : N, 16·6. $C_{12}H_{21}O_3N_3$ requires N, 16·4 per cent).

Ethyl 5-*Methyl*cyclo*hexanone-2-acetate*, obtained by esterifying 5-methyl*cyclo*hexanone-2-acetic acid (10 g.) collected at 127°/5 mm., yield 9 g. (Found : C, 66·4 ; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·6 ; H, 9·0 per cent).

The *semicarbazone*, crystallised from alcohol, m. p. 174-75°. (Found : N, 16·7. $C_{12}H_{21}O_3N_3$ requires N, 16·4 per cent).

Ethyl 6-*Methyl*cyclo*hexanone-2-acetate*, obtained by esterfying 6-methyl*cyclo*hexanone-2-acetic acid, distilled at 125°-130°/8 mm. (Found : C, 66·6 ; H, 9·0. $C_{11}H_{18}O_3$ requires C, 66·6 ; H, 9·0 per cent).

Ethyl 1-Hydroxy-4-methylhexahydrodiphenyl-2-acetate.—PhMgBr (from 5·5 c.c. of bromobenzene and 1·3 g. of Mg) was added drop by drop to an ethereal solution of 4-methyl*cyclo*hexanone-2-acetate (10·5 g.), kept cool by means of ice. The reaction mixture was left overnight and the product decomposed by means of dilute sulphuric acid. After removing ether it was distilled at 168-178°/8 mm., yield 4 g. (Found : C, 74·2 ; H, 8·5. $C_{17}H_{24}O_3$ requires C, 73·9 ; H, 8·6 per cent).

Ethyl 1-Hydroxy-5-methylhexahydrodiphenyl-2-acetate was obtained by the action of PhMgBr on 5-methyl*cyclo*hexanone-2-acetate (10 g.), b.p. 165-75°/7 mm., yield 3 g. (Found : C, 74·4; H, 8·7. $C_{17}H_{24}O_3$ requires C, 73·9 ; H, 8·6 per cent).

Ethyl 1-Hydroxy-6-methylhexahydrodiphenyl-2-acetate was obtained by the action of PhMgBr on 6-methyl*cyclo*hexanone-2-acetate, b.p. 160-70°/7mm. (Found : C, 74·3; H, 8·8. $C_{17}H_{24}O_3$ requires C, 73·9; H, 8·6 per cent).

Ethyl 4-Methyldiphenyl-2-acetate.—Ethyl 1-hydroxy-4-methylhexahydrodiphenyl-2-acetate was heated with sulphur for 4 to 5 hours at 200-240° and the product after washing with caustic alkali was distilled at 160-67°/6 mm. (Found : C, 79·9; H, 7·0. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·08 per cent).

Ethyl 6-Methyldiphenyl-2-acetate was obtained by heating ethyl 1-hydroxy-5-methylhexahydrodiphenyl-2-acetate with sulphur as above, b.p. 160-163°/9mm. (Found: C, 80·0; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·08 per cent).

Ethyl 5-Methyldiphenyl-2-acetate was obtained by heating ethyl 1-hydroxy-5-methylhexahydrodiphenyl-2-acetate with sulphur as described above, b.p. 160-65°/6mm. (Found: C, 80·1; H, 7·2. $C_{18}H_{17}O_2$ requires C, 80·3; H, 7·08 per cent).

Ethyl Hexahydrodiphenyl-2-acetate.—Thionyl chloride (17 g.) was added slowly to a well-stirred ice-cold mixture of ethyl 1-hydroxyhexahydrodiphenyl-2-acetate (32 g.), anhydrous ether (70 c.c.), and pyridine (29 c.c.). Stirring and cooling were continued for 2 hours, the solution was then poured into water and the product after washing with dilute caustic alkali was extracted with ether and the ethereal solution was washed, dried, and distilled, b.p. 165-75°/7 mm. (Found : C, 78·1 ; H, 8·2. $C_{16}H_{20}O_2$ requires C, 78·6 ; H, 8·3 per cent). 5 G. of the substance in alcohol (40 c.c.) were shaken for 8 days with platinum oxide (0·1 g.) in an atmosphere of hydrogen when the theoretical quantity of hydrogen was absorbed. Ethyl hexahydrodiphenyl-2-acetate boiled at 168-72°/8 mm. (Found : C, 78·3; H, 8·8. $C_{16}H_{22}O_2$ requires C, 78·1 ; H, 8·8 per cent).

Hexahydrodiphenyl-2-acetic Acid was obtained by refluxing ethyl hexahydrodiphenyl-2-acetate with alcoholic potash for 2 hours. The alcohol was distilled off and after dilution the unchanged ester was removed by ether. The aqueous layer was concentrated and after acidification the free acid was extracted with ether, the ether removed, the product kept in a desiccator for 2 days when it solidified. It was finally crystallised from dilute acetic acid as colourless needles, m.p. 168-70°. (Found : C, 76·7 ; H, 8·3. Calc. for $C_{14}H_{18}O_2$: C, 77·0; H, 8·3 per cent).

Lactone of Ethyl 1-Hydroxy-2-acetic acid-4-methylhexahydrodiphenyl-2-carboxylate.—PhMgBr (from 5 c.c. bromobenzene and 1·2 g. of Mg.) was added drop by drop to an ethereal solution of diethyl-4-methyl*cyclo*hexanone-2-carboxylate-2-acetate (13 g.) kept cool by means of ice.

A gelationous precipitate separated and the reaction mixture was left overnight and then decomposed by means of dilute sulphuric acid. After removing the ether it was subjected to fractional distillation in vacuum and the product collecting at 200-220°/7 mm., was found to solidify at room temperature. It crystallised from alcohol, m.p. 112°, yield 4 g. (Found : C, 71·4; H, 7·2. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·2 per cent).

Lactone of Ethyl 1-Hydroxy-5-methyl-2-acetic acid-hexahydrodiphenyl-2-carboxylate was obtained by the action of PhMgBr on diethyl 5-methyl*cyclc*hexanone-2-carboxylate (13 g.) by a method similar to that described acove, b.p. 210-20°/7mm., yield 4 g. (Found: C, 71·3; H, 7·1. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·2 per cent).

Lactone of Ethyl 1-Hydroxy-2-acetic acid-6-methylhexahydrodiphenyl-2-carboxylate was obtained by the action of PhMgBr on diethyl 6-methyl*cyclo*hexanone-2-carboxylate-2-acetate, b. p. 205-15°/mm. (Found : C, 71·1; H, 7·4. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·2 per cent).

In conclusion the author desires to express his sincere thanks to Professor Dr. P. C. Mitter for encouragement and advice during the course of this work.

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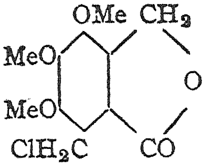
On Phthalide Formation.

By Prafulla Kumar Paul.

Prior to the observation of Perkin that formaldehyde condenses directly with *m*-methoxy-benzoic acid derivatives in presence of concentrated hydrochloric acid (*J. Chem. Soc.*, 1925, **127**, 197) to yield phthalide, there was the Fritsch reaction (*Annalen*, 1897, **296**, 344; 1898, **301**, 352), a very round about way of synthesising similarly constituted compounds.

The present investigation was undertaken with a view to effect a synthesis of cotarnic acid and myristicinic acid methyl ester was subjected to the Fritsch reaction, but the methylene-dioxy group was found to be unstable towards 90% sulphuric acid, and Perkin's method of phthalide formation also led to unworkable tarry products. Perkin's method as modified by Roy and Robinson (*J. Chem. Soc.*, 1925, **127**, 1621) was next tried, but the reaction product from both gallic acid trimethyl ether and myristicinic acid was chloromethyl phthalide (I).



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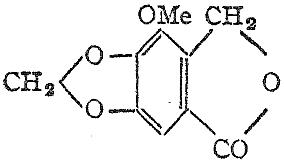

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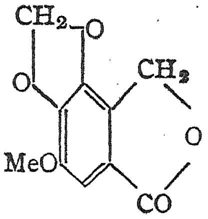

(III)

The chloromethyl phthalide derivatives gave with potassium cyanide in alcoholic solution the respective cyanomethyl phthalides which on hydrolysis gave the corresponding phenyl acetic acid derivatives.

But if in place of glacial acetic acid used by Roy and Robinson in their modification of Perkin's method, water be used simple phthalides are obtained and the phthalide, thus obtained from gallic acid trimethyl ether, was found to be identical with that described by Meldrum (*J. Chem. Soc.*, 1920, **117**, 964). The phthalide obtained from myristicinic acid may have either of the structures (II) and (III), but owing to the failure of the oxidation experiments the constitution of the product could not be settled.

alcohol was distilled off and after dilution the unchanged ester was removed by ether. The aqueous layer was concentrated and after acidification the free acid was extracted with ether, the ether removed, the product kept in a desiccator for 2 days when it solidified. It was finally crystallised from dilute acetic acid as colourless needles, m.p. 168-70°. (Found : C, 76·7 ; H, 8·3. Calc. for $C_{14}H_{18}O_2$: C, 77·0; H, 8·3 per cent).

Lactone of Ethyl 1-Hydroxy-2-acetic acid-4-methylhexahydrodiphenyl-2-carboxylate.—PhMgBr (from 5 c.c. bromobenzene and 1·2 g. of Mg.) was added drop by drop to an ethereal solution of diethyl-4-methyl*cyclo*hexanone-2-carboxylate-2-acetate (13 g.) kept cool by means of ice.

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Lactone of Ethyl 1-Hydroxy-5-methyl-2-acetic acid-hexahydrodiphenyl-2-carboxylate was obtained by the action of PhMgBr on diethyl 5-methyl*cycl*chexanone-2-carboxylate (13 g.) by a method similar to that described acove, b.p. 210-20°/7mm., yield 4 g. (Found: C, 71·3; H, 7·1. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·2 per cent).

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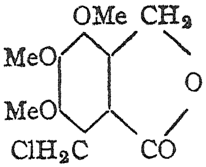
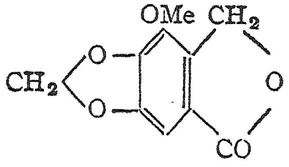
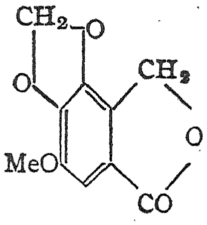
By Prafulla Kumar Paul.

Prior to the observation of Perkin that formaldehyde condenses directly with *m*-methoxy-benzoic acid derivatives in presence of concentrated hydrochloric acid (*J. Chem. Soc.*, 1925, **127**, 197) to yield phthalide, there was the Fritsch reaction (*Annalen*, 1897, **296**, 344; 1898, **301**, 352), a very round about way of synthesising similarly constituted compounds.

The present investigation was undertaken with a view to effect a synthesis of cotarnic acid and myristicinic acid methyl ester was subjected to the Fritsch reaction, but the methylene-dioxy group was found to be unstable towards 90% sulphuric acid, and Perkin's method of phthalide formation also led to unworkable tarry products. Perkin's method as modified by Roy and Robinson (*J. Chem. Soc.*, 1925, **127**, 1621) was next tried, but the reaction product from both gallic acid trimethyl ether and myristicinic acid was chloromethyl phthalide (I).


(I)


(II)


(III)

The chloromethyl phthalide derivatives gave with potassium cyanide in alcoholic solution the respective cyanomethyl phthalides which on hydrolysis gave the corresponding phenyl acetic acid derivatives.

But if in place of glacial acetic acid used by Roy and Robinson in their modification of Perkin's method, water be used simple phthalides are obtained and the phthalide, thus obtained from gallic acid trimethyl ether, was found to be identical with that described by Meldrum (*J. Chem. Soc.*, 1920, **117**, 964). The phthalide obtained from myristicinic acid may have either of the structures (II) and (III), but owing to the failure of the oxidation experiments the constitution of the product could not be settled.

In conclusion, it may be remarked that *m*-methoxy-benzoic acid derivatives, having an additional *p*-orienting group chiefly the methoxyl, yield by Roy and Robinson's method chloromethyl phthalide provided the *p*-position to the additional methoxyl group is free.

EXPERIMENTAL.

Gallic Acid Series.

3: 4: 5-*Trimethoxy-2-chloromethylphthalide.*—Gallic acid trimethyl ether (10 g.), glacial acetic acid (50 c.c.), fuming hydrochloric acid (40 c. c.) and 40% formaldehyde solution (12·5 c.c.) were heated under reflux on a steam-bath for 3-4 hours, when the reaction mixture turned deep brown. The reaction product was precipitated by diluting the reaction mixture with a large volume of water, filtered, washed with water and treated with dilute sodium bicarbonate solution, when the unreacted acid dissolved leaving the chloromethyl phthalide derivative as an almost colourless powder. It crystallises in colourless needles, m.p. 86°. (Found: Cl, 12·86 ; OMe, 33·6. $C_{12}H_{13}O_5Cl$ requires Cl, 13·02; OMe, 34·12 per cent).

3 : 4 : 5-*Trimethoxy-2-cyanomethylphthalide.*—The above compound (5·5 g.) was heated with potassium cyanide (1·6 g.) and alcohol (4 c.c.) on a steam-bath under reflux for 4 hours, when the reaction was complete. The reaction product was obtained by diluting the reaction mixture with water. It crystallises from alcohol in stout prisms, m.p. 103°. (Found : N, 4·97. $C_{13}H_{13}O_5N$ requires N, 5·32 per cent).

3 : 4 : 5-*Trimethoxy-2-phenylacetic Acid.*—The foregoing cyanomethyl phthalide (5 g.) was refluxed with 10% caustic soda solution (100 c.c.) for 8-9 hours, when evolution of ammonia ceased and the hydrolysis was complete. The product of hydrolysis was then separated by acidification with hydrochloric acid and boiling for 10 minutes, cooling and filtering. The filtered solid was then triturated in a mortar with sodium bicarbonate solution, the solution filtered and the filtrate acidified with excess of hydrochloric acid. It was then crystallised from dilute alcohol, m. p. 126°. (Found : C, 55·08 ; H, 5·13. $C_{13}H_{14}O_7$ requires C, 55·31 ; H, 4·96 per cent).

Myristicinic Acid Series.

3 : 4- (or 4 : 5)-*Methylenedioxy*-5- (*or* 3)-*methoxy-2-chloromethyl phthalide.*—Myristicinic acid (10 g.), glacial acetic acid (50 c.c.),

fuming hydrochloric acid (40 c.c.) and 40% formaldehyde solution (12·5 c.c.) were mixed together and heated on a steam-bath for 3-4 hours, animal charcoal was then added and heating continued for another ½ hour, the solution was then filtered when the product of the reaction crystallised out. It was collected, washed with dilute sodium bicarbonate solution and finally crystallised from alcohol in slightly brownish needles, m.p. 133°-134°. (Found : Cl, 13·59. $C_{11}H_9O_5Cl$ requires Cl, 13·84 per cent).

Cyanomethyl-phthalide.—The above chloromethyl phthalide (5 g.), potassium cyanide (1·5 g.) and alcohol (5 c.c.) were mixed together and heated under reflux on a steam-bath for 3-4 hours and then the product of the reaction was mixed with water, cooled and filtered. The cyanomethyl derivative, thus obtained, was then crystallised from benzine mixed with a little benzene in beautiful wooly needles, m.p. 146°-47°. (Found : N, 5·74. $C_{12}H_9O_5N$ requires N, 5·66 per cent).

Phenylacetic Acid.—The above cyanomethyl phthalide (5 g.) was boiled under reflux with 10% caustic soda solution (100 c.c.) till there was no evolution of ammonia. The product of hydrolysis was then acidified with concentrated hydrochloric acid (75 c.c.) and boiled for ½ hour and cooled when the phenyl acetic acid derivative was precipitated. The precipitate was then dissolved in dilute sodium bicarbonate solution, filtered and the filtrate acidified with hydrochloric acid. It was then collected and crystallised from alcohol in prismatic needles, m.p. 211°-12°. (Found : C, 53·86 ; H, 4·02. $C_{12}H_{10}O_7$ requires C, 54·13 ; H, 3·75 per cent).

Phthalide from Myristicinic Acid.—Myristicinic acid (10 g.), concentrated hydrochloric acid (10 c.c.), formaldehyde (40%, 12·5 c.c.) and water (50 c.c.) were boiled under reflux for ½ hour when a tarry product was found to adhere to the walls of the vessel. The clear liquid was decanted and the tarry product was repeatedly extracted with boiling water, when the phthalide separated on cooling. It was filtered, washed with sodium bicarbonate solution and crystallised from alcohol in stout needles, m.p. 181°. (Found : C, 57·62 ; H, 4·13. $C_{10}H_8O_5$ requires C, 57·69 ; H, 3·84 per cent).

I wish to express my grateful thanks to the authorities of the Company for their kind permission to carry out the work.

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Preparation and Properties of Highly Concentrated Sols. Part V. Stannic Hydroxide Sols.

By N. R. Dhar and Ch. I. Varadanam.

In previous publications (*J. Indian Chem. Soc.*, 1932, 9, 315, 441, 455; *Kolloid Z.*, 1935, 71, 173) from these laboratories we have reported the preparation and properties of highly concentrated sols of aluminium, iron, chromium, zirconium, and thorium hydroxides, vanadium pentoxide and silicic and molybdic acids. In the present paper, we are communicating our results on highly concentrated stannic hydroxide sols.

Preparation of the Sol.

Stannic chloride (hydrated crystals 45 g.) was dissolved in 100 c.c. of water and very strong ammonium hydroxide was gradually added with constant stirring. Heat is evolved in the reaction and therefore the beaker was kept in a cold water-bath. When a sufficient quantity of ammonium hydroxide had been added, a viscous gel was obtained. It was repeatedly washed with distilled water, and then it was peptised with a minimum quantity of strong ammonium hydroxide. The sample, washed 14 times with water, took about 4 hours to give a clear sol.

The sol thus prepared was further concentrated by slow evaporation. At a certain stage a scum appeared on the surface, and on further concentration, a jelly was formed. The sol at this stage, before the formation of the jelly contained 68·4 g. SnO_2 per litre. The sols of the following concentrations were obtained :

	Prepared in the cold.	Concentrated by evaporation.
Sol I	65·4 g. /litre	68·4 g. /litre
Sol II. (purer)	45·0	80·9

These sols on dialysis for about two days form transparent jellies in the dialyser. A sol obtained by washing the gel for three days contained as much as 90·2 g. of SnO_2 per litre. This sol was also converted into a jelly when left exposed to atmosphere. The concentrations of the sol prepared over sulphuric acid in a desiccator also gave 89·8 g. SnO_2 per litre.

Coagulations of the Sol.

It was difficult to study the coagulation of very highly concentrated sols by the addition of electrolytes. The coagulation of the following sols has been studied.

TABLE I.

Amount of sol taken = 0·5 c.c. Total volume = 15 c.c. Time of observation = 1 hour.

Days dialysed.	Electrolyte.	Ppt. conc.	Conc. of the sol in SnO_2/litre.
2	KCl	0·07330	40·6 g.
	$BaCl_2$	0·00052	
	$Al(NO_3)_3$	0·0004	
5	KCl	0·06	40·2
	$BaCl_2$	0·00038	
	$Al(NO_3)_3$	0·00028	
7	KCl	0·0269	41·2
	$BaCl_2$	0·00024	
	$Al(NO_3)_3$	0·00018	
10	KCl	0·01133	42·4
	$BaCl_2$	0·00016	
	$Al(NO_3)_3$	0·00014	

The precipitating ratios are given in the following table. The value from the trivalent ion has been taken as unity.

TABLE II.

	The sols dialysed for			
	2 days.	5 days.	7 days.	10 days.
Monovalent	183·4	169·2	145·2	78·6
Bivalent	1·302	1·364	1·296	1·11
Trivalent	1·00	1·0	1·00	1·00

It will be seen from these figures that the sols, which have been dialysed for a longer time, require smaller amounts of electrolyte for coagulation. Moreover, the ratio of the precipitating concentrations of mono, bi and trivalent ions decreases continuously as the dialysis proceeds, that is, as the purity of the sol increases. Similar results were obtained by Dhar and collaborators on other highly concentrated sols, and as the purity increases, the precipitation concentrations approach the ratios required by the expression of Chakravarti, Ghosh and Dhar (*J. Phys. Chem.*, 1930, 34, 330).

$$N_1 : N_2 : N_3 = 1 : \tfrac{1}{2}\alpha : \tfrac{1}{3}\alpha^2 : \ldots$$

$$\text{Where } \alpha = e^{\frac{-q\rho/DR}{kT}}.$$

It may also be noted here, that the coagulum obtained from an impure sol is opalescent, whereas that from a pure sol is transparent.

Purity of the Sol.

The concentrated sols of stannic hydroxide contain traces of chloride ions, and a sufficient amount of ammonium hydroxide as impurity, as shown from the following table. Ammonia was estimated colourimetrically by Nessler's reagent, and chloride gravimetrically as AgCl.

TABLE III.

Days dialysed	Conc. of SnO_2 per litre.	Cl′ ion per litre.	Conc. of ammonia.
2	40·6 g.	0·5494 g.	0·1105 *N*
5	40·2	0·0301	0·0458
7	41·2	Traces	0·0371
10	42·4	”	0·0236

Viscosity of Sols.

It was reported in previous publications, that the highly concentrated sols of iron, chromium, aluminium, thorium and zirconium hydroxides possess a very high viscosity, and also that the viscosity markedly increases with the purity of the sols. However, the stannic hydroxide sols do not show very high viscosity even on dialysis.

With continued dialysis, the concentration of the sol falls markedly. Some of the results are given in the following table.

TABLE IV.

Temperature = 30°. Viscosity of water at 30°0—·00803.

Days of dialysis.	Density.	Conc. of SnO_2 per litre.	Viscosity.
Undialysed sol.	1·1026	90·4 g.	0·01018
1	1·084	85·4	0·01018
2	1·076	76·6	0·01193
3	1·069	69·7	0·01245
5	1·059	59·0	0·01294
7	1·047	50·2	0·01218
9	1·042	40·4	0·01213

It has been observed that even a very pure sol, which sets to a jelly on standing, does not possess a high viscosity as was observed with other concentrated sols. The ageing effect of the sol on the viscosity of undialysed and dialysed sols is also not marked, except in those cases where the sol sets to a gel on standing for some days.

Jelly Formation with Stannic Hydroxide.

Weiser (*J. Phys. Chem.*, 1922, **26**, 681) has studied the jelly formation of stannic hydroxide. The concentrated sols which we have obtained give a transparent jelly when treated with hydrochloric acid, potassium and barium chlorides. Some of the jellies are markedly thixotropic and are converted to sols when shaken, but again set to jellies on standing. Some of the results are given in Table V.

TABLE V.

Concentration of the sol dialysed for 19 days = 37·2 g. of SnO_2/litre. Amounts of the sol taken = 4 c.c. Total volume = 5 c.c.

Concentration of KCl(*M*)	0·003105	0·003726	0·004347	0·004968	0·005589	0·006210
Time of gelation in minutes.	175	72	2·3	10	·5	2
Thixotropic time in minutes for resetting.	5	3	1	...	...	...

Electric Conductivity of the Sols.

We have also studied the electric conductivities of stannic hydroxide sols dialysed for a different number of days, and also the influence of dilution and temperature on conductivity of a particular sol. The results are given below :

TABLE VI.

Temperature = 35°.

Days of dialysis.	Concentration of SnO_2/litre.	Sp. conductivity in mhos $\times 10^{-4}$.	Days of dialysis.	Concentration of SnO_2/litre.	Sp. conductivity in mhos $\times 10^{-4}$.
1	85·4 g.	29·85	5	29·5	6·13
,,	47·7	15·83	7	50·2	9·14
2	76·6	20·12	,,	25·1	4·81
,,	38·3	12·86	9	42·4	7·55
3	69·7	16·46	,,	21·2	3·72
,,	34·8	8·33	11	37·7	6·56
5	59·0	14·06	,,	18·8	2·66

TABLE VII.

Temperature = 35°.

Dilution.	Sp. conductivity in mhos × 10^{-4}.	Sp. conductivity × 10^{-4} as calculated.
90·2 g./litre (A)	50·05	50·05
A/2	30·69	61·38
A/4	19·49	77·96
A/8	11·62	90·82
A/16	6·86	109·8
A/32	5·47	175·5

TABLE VIII.

Concentration of the two days' dialysed sol = 82·2 g. of SnO_2/litre.

Temp.	Sp. conductivity × 10^{-4}.
25°	19·09
35°	22·96
45°	26·03

From these results, it will be seen that on dialysis, as the purity increases, the conductivity of the sol decreases. The influence of temperature on the conductivity is also regular. The results in the Table VII show that the conductivity multiplied by the dilution of the sol goes on increasing as the dilution proceeds.

An attempt was also made to study the cataphoresis of the stannic hydroxide particles by the improved method of Mukherjee, but the difficulty was in procuring a sharp boundary in a non-opalescent colourless sol of stannic hydroxide. Various indicators, as phenolphthalein and methylene blue were tried. No indicator was necessary for the undialysed sol which was sufficiently opalescent to give a sharp bounary. The results are given in Table IX. The cataphoretic movement was extremely slow.

TABLE IX.

Voltage applied = 170. Time = 30 min.

Days dialysed.	Conc. of SnO_2/litre.	Conc. of KCl as the upper liquid.	Movement of Left limb.	Movement of Right limb.
undialysed	40·5 g.	$N/5$	3 mm.	3 mm.
			Voltage	reversed
	,,	,,	3 mm.	3 mm.
1 day	37·3	$N/16$	3 mm.	4 mm.
			Voltage	reversed
	,,	,,	4 mm.	3 mm.

SUMMARY.

1. A highly concentrated sol of negatively charged stannic hydroxide has been prepared of a concentration of 98·4 grams SnO_2 per litre by peptising well washed stannic hydroxide with concentrated ammonia, and evaporating the sol on a water-bath. An attempt to further concentrate it, resulted in the formation of a jelly.

2. The coagulation of concentrated sols has been studied, and it was found that as the purity increases on dialysis, the ratio of precipitating concentrations of mono, bi and trivalent ions goes on decreasing.

3. The stannic hydroxide sols do not possess so high viscosities as iron, chromium and thorium hydroxides. The electric conductivities have also been studied.

4. The colloidal particles of stannic hydroxide show a very slow cataphoretic movement.

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Derivatives of 1-Hydroxy-2-naphthoic Acid. Part I. 4-Halogeno-1-hydroxy-2-naphthoic Acid and their Derivatives.

By G. V. Jadhav, S. N. Rao and N. W. Hirwe.

Since much work has been done in these laboratories on derivatives of salicylic acid, it was thought interesting to examine the reactions of 1-hydroxy-2-naphthoic acid, which can be regarded as a salicylic acid with the 3- and 4- positions fused with a benzene molecule. Thus, its behaviour may be analogous with the 3- substituted derivatives of salicylic acid, since the position 4 does not play an important rôle, being outside the directing influences.

Thus, the acid chloride of the naphthoic acid is as easily obtained (Anschutz and co-workers, *Annalen*, 1906, **346**, 361) as that of *o*-cresotic acid or salicylic acid with the 3- position occupied, either by chloro, nitro (Anschutz, *Ber.*, 1897, **30**, 222; *Annalen*, 1906, **346**, 342, 336), or bromo group (Hirwe, *unpublished work*). The esters of the 3-substituted salicylic acids are obtained through the silver salts or through the acid chlorides (Anschutz and Anspach, *Annalen*, 1906, **346**, 313; Hübner, *ibid.*, 1879, **195**, 34; Anschutz and co-workers, *ibid.*, 1906, **346**, 343). With the naphthoic acid it has been found very difficult to get the ester directly (Kauffmann and Egner, *Ber.*, 1913, **46**, 3782).

To extend the above analogies further, the naphthoic acid was halogenated and the behaviour of these acids studied. These halogeno acids were obtained by the substitution of the sulphonic acid group in 4-sulpho-1-hydroxy-2-naphthoic acid (Konig, *Ber.*, 1889, **22**, 787; 1890, **23**, 806) by the halogens and the halogen-free phthalic acid, obtained on oxidation of these acids, further confirms their structures.

The 4-halogenonaphthoic acids gave the naphthoyl chloride with phosphorus pentachloride as easily as the 3:5-disubstituted salicylic acids (Anschutz, *loc. cit.*).

Various derivatives of these acids have been described. The work is being extended.

EXPERIMENTAL.

4-Bromo-1-hydroxy-2-naphthoic Acid.—Bromine (2·5 g.) in acetic acid (10 c.c.) was gradually added in the cold to 4-sulpho-1-hydroxy-

2-naphthoic acid (5 g.) suspended in acetic acid (50 c.c.) and the mixture then heated at 100° for ½ hour to complete the reaction. The bromo-acid (3·6 g.) crystallised from acetic acid in white needles, m.p. 240-41° (decomp.), mixed m.p. with the acid prepared according to Weil (*Ber.*, 1911, **44**, 3060; *cf.* Schmitt and Burkard, *Ber.*, 1887, **20**, 2700). (Found: Br, 30·1. Calc. for $C_{11}H_7O_3$ Br : Br, 30·0 per cent).

Phthalic acid (m.p. 197°) was obtained, when the bromo acid (2 g.) was heated with nitric acid (*d* 1·16, 15 c.c.) in a sealed tube at 150-60° for 8 hours.

4-*Bromo*-1-*hydroxy*-2-*naphthoyl Chloride*.—A mixture of the above acid (3 g.), dry benzene (4 c.c.), dry light petroleum ether (10 c.c.) and phosphorus pentachloride (3 g.) was gently heated on the water-bath, until a clear yellow solution was obtained. The naphthoyl chloride separated on cooling as yellow needles, which were collected and washed with dry light petroleum ether and dried over phosphorus pentoxide, m.p. 118-9°. [Found: Total halogen calc. as Cl, 28·5 ; by analysis of silver halides Cl, 12·4 ; Br, 27·8. $C_{11}H_6O_2BrCl$ requires Cl, 12·4; Br, 28·0 per cent].

4-*Chloro*-1-*hydroxy*-2-*naphthoic Acid*.—Dry chlorine gas (1 g.) was passed at 65°, with constant stirring, through 4-sulpho-1-hydroxy-2-naphthoic acid (5 g.) suspended in acetic acid (25 c.c.). The solid (1·4 g.) crystallised from acetic acid in colourless needles, m.p. 232-33° (decomp.), mixed m.p. with the acid prepared according to Reissert (*Ber.*, 1911, **44**, 866; *cf.* Weil and Heerdt, *Ber.*, 1922, **55**, 288 ; Weil, *Ber.*, 1911, **44**, 3061). (Found: Cl, 15·9. Calc. for $C_{11}H_7O_3Cl$: Cl, 16·0 per cent).

On oxidation of the acid, in the same way as in the case of 4-bromo-acid, phthalic acid was obtained.

4-*Chloro*-1-*hydroxy*-2-*naphthoyl Chloride* was prepared in the same way as its bromo isomer in fine yellow needles, m.p. 121-22°. (Found: Cl, 29·4. $C_{11}H_6O_2Cl_2$ requires Cl, 29·5 per cent).

The phenyl and β-naphthyl esters of these halogeno-acids were prepared by heating a mixture of the acid with the respective phenol and phosphorus oxychloride at 140-150° to a clear solution and then treating with water. Alkyl esters were obtained by heating either the silver salt of the acid or the naphthoyl chloride with the respective alkyl iodide or alcohol. The arylamides were prepared by treating the benzene solution of the naphthoyl chloride with the respective amine.

TABLE I.

Derivatives of 4-Bromo-1-hydroxy-2-naphthoic Acid.

Name.	Formula.	Crystallised from.	Appearance.	M.p.	Analysis. Found.	Analysis. Calc.
Sodium salt	$C_{11}H_6O_3BrNa, 2\frac{1}{2}\ H_2O$	Water	Shining needles		Na, 6·9% H_2O, 13·8	6·9 % 13·5
Potassium salt	$C_{11}H_6O_3BrK$	,,	Pinkish needles		K, 12·7	12·8
Phenyl ester	$C_{17}H_{11}O_3Br$	Acetone and alcohol	Shining needles	104-5°	Br, 23·3	23·3
β-Naphthyl ester	$C_{21}H_{13}O_3Br$	Acetic acid	Long white needles	183-84°	20·4	20·4
Methyl ester	$C_{12}H_9O_3Br$	Alcohol	Small white needles	121-22°	28·2	28·5
Ethyl ester	$C_{13}H_{11}O_3Br$	,,	Grey needles	86-87°	27·2	27·1
Anilide	$C_{17}H_{12}O_2NBr$	,,	White needles	164-65°	23·1	23·4
o-Toluidide	$C_{18}H_{14}O_2NBr$	,,	,, ,,	164-65°	22·8	22·5
m-Toluidide	,,	Acetone and alcohol	Pinkish white needles	202-3°	22·6	22·5
p-Toluidide	,,	,,	White needles	150-51°	22·8	22·5

TABLE II.

Derivatives of 4-Chloro-1-hydroxy-2-naphthoic Acid.

Name.	Formula.	Crystallised from.	Appearance.	M. p.	Analysis. Found.	Analysis. Req.
Potassium salt	$C_{11}H_6O_3ClK$	Water	Grey needles		K, 14·8%	15·0%
Phenyl ester	$C_{17}H_{11}O_3Cl$	Acetone and alcohol	Pale yellow plates	103-4°	Cl, 11·9	11·9
β-Naphthyl ester	$C_{21}H_{13}O_3Cl$	Acetic acid	White needles	186-87°	9·9	10·2
Methyl ester	$C_{12}H_9O_3Cl$	Alcohol	,, ,,	120-21°	15·0	15·0
Ethyl ester	$C_{13}H_{11}O_3Cl$	,,	Grey needles	92-93°	14·2	14·2
Anilide	$C_{17}H_{12}O_2NCl$	,,	White needles	180-81°	Cl, 12·1 N (micro), 4·6	12·0 4·7
o-Toluidide	$C_{18}H_{14}O_2NCl$	Acetic acid	,, ,,	148-49°	Cl, 11·3	11·4
m-Toluidide	,,	,,	Pale yellow needles	188-89°	11·6	11·4
p-Toluidide	,,	,,	Shining grey needles	143-44°	11·2	11·4

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The Chemical Examination of *Solanum Xanthocarpum*, Schard and Wendle. Part I. The Constituents of the Oil from the Seeds.

BY MAHADEO PRASAD GUPTA AND SIKHIBHUSHAN DUTT.

Solanum xanthocarpum (N. O. *Solanaceæ*) commonly known as Bhatkatya in Hindi and Kanta-Kari in Sanskrit and in Bengali is common throughout India. The description of the plant and its medicinal properties are given in detail in Dymock ("Pharmacographica Indica," 1891, II, 557) and Basu and Kirtikar ("Indian Medicinal plants," 1918, II, 896). The plant is of great importance in Hindu medicine, as being useful in fever, cough, asthma, constiveness, heart disease, toothache, etc.

So far scarcely any work of a chemical nature has been done on the fruits and the present investigation was undertaken to put the fruits to a thorough chemical examination. The benzene extract of the seeds yielded an oil of greenish yellow colour and some crystalline matter. The purification and constitution of the crystalline matter is being investigated.

EXPERIMENTAL.

Fresh fruits (33·15 kg.) were dried, crushed and the pericarp separated mechanically. The dry seeds constituted 20·71 %, and the pericarp 4·62% and the moisture 74·67% of the fresh fruits by weight. The ash of the crushed fruit contained 44·38% of water-soluble and 55·62% of water-insoluble inorganic material, and contained the following positive and negative radicals : potassium, iron, calcium, (in traces), magnesium, silica, carbonate, chloride, sulphate and phosphate.

Crushed seeds (30 g.) were successively extracted with various solvents in a Soxhlet's apparatus and the extracts were dried at 100° when the following results were obtained.

Benzene extract (19·28%).—The extract was a greenish yellow oil which disposited some crystalline matter on standing.

Chloroform extract (3·2%).—The extract was of yellowish brown colour and gave positive tests for alkaloids, soluble in acids, and also in caustic soda with yellow colour, forming neutral as well as basic lead salts and giving no colour with ferric chloride.

The Ethyl acetate extract (1·65%), *the acetone* (1·62%) as well as the *alcoholic extracts* (3·39%) were of yellowish brown colour, and showed the same reactions as the chloroform extract and were very slightly bitter in taste.

Extraction of the Oil—Powdered seeds (2·2 kg.) were exhaustively extracted with benzene when 418 g. of a greenish yellow oil having characteristic odour were obtained. The crude oil was purified with animal charcoal and Fuller's earth. The oil was of bright yellow colour when viewed in thin layers and greenish yellow in thick layers.

Examination of the Oil.—The oil does not contain nitrogen or sulphur. It burns with slightly smoky flame and is slightly optically active showing a rotation of $[\alpha]^{32}_{D} = -1{\cdot}35$ in chloroform. On examination it was found to be semi-drying ; $d^{27°}$, 0·9240 ; it does not solidify upto -11° but becomes thick ; acid value, 70·78 ; acetyl value, 40·4 : saponification value, 182·5 ; Hehner's value, 94·9 ; iodine value, 124·3 ; unsaponifiable matter, 1·2%.

150 G. of the oil were saponified in the usual manner with alcoholic potash and the unsaponifiable matter extracted with ether. The fatty acids were then extracted in the usual manner. The mixed fatty acids have the following constants : Consistency, liquid ; $d^{27°}$, 0·8775 ; neutralisation value, 173·9 ; mean M.W., 322·7 ; iodine value, 121·37.

The mixture of the fatty acids (52 g.) was then separated into saturated (solid) and unsaturated (liquid) acids by the Twitchell's lead salt alcohol method (*J. Ind. Eng. Chem.*, 1921, **13**, 806). During the separation of saturated and unsaturated acids, a small quantity of resinous acid insoluble in ether also separated and it is to their presence that the mean molecular weight of the mixed acids is so high. Table I gives the percentage, iodine value and the mean molecular weight of the saturated and unsaturated acids.

TABLE I.

Acids.	In mixed acids.	In the oil.	Iodine value.	Mean M. W.
Saturated	16·62%	15·77%	4·24	285
Unsaturated	83·38	79·11	129·7	279·8

Examination of Unsaturated Acids.—The unsaturated acids, separated by the above method, showed beautiful green fluorescence, and their constituents were determined quantitatively by the method of Jmaieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 1197) by preparing their bromine addition products. The hexabromo derivative of linolenic acid is insoluble in cold ether ; since no precipitate insoluble in ether was formed, the absence of linolenic acid was confirmed. The ether-soluble portion was dissolved in petroleum ether and cooled when crystals of linolic tetrabromide (m.p. 113-14°) were separated showing the presence of linolic acid. The residue was evaporated to dryness and the bromine content estimated. Table II contains the results of the analysis of the bromine addition products.

TABLE II.

Weight of unsaturated acids taken	5·6192 g.
Linolic tetrabromide (insoluble in petroleum ether)	2·8294
Residue (dibromide and tetrabromide)	7·4552
Bromine content of the residue	42·33%
Dibromo-oleic acid in residue	64·1% or 4·7800 g.
Tetrabromolinolic acid in residue	35·9% or 2·6770 g.
Total tetrabromide found	5·5064 g.
Linolic acid equivalent to tetrabromide	45·74% or 2·5700 g.
Oleic acid equivalent to dibromide	54·26% or 3·0490 g.

The proportions of the linolic and oleic acids in the unsaturated acids was also determined from the iodine value of the liquid acids.

Table III (*a*) contains the percentage of the linolic and oleic acids in the unsaturated acids, and the percentage of their glycerides in-original oil calculated by bromine addition method, and Table III (*b*) percentages calculated by iodine method.

TABLE III (*a*)

Acid.	Found by bromine addition products.	In the total fatty acids.	In the original oil.
Oleic acid	54·26%	45·23%	42·93%
Linolic acid	45·74	38·14	36·19

TABLE III (*b*)

Acids.	Calculated by iodine value.	In the total fatty acids.	In the original oil.
Oleic	56·38%	47·00	46·71
Linolic	43·62	36·40	34·55

The theoretical iodine value of a mixture consisting of 54·26% of oleic acid and 45·74% of linolic acid is 131·7, which agrees fairly well with the observed iodine value of the unsaturated acids (129·7).

Examination of the Saturated Acids.—The saturated acids separated by the lead salt alcohol method were freed from traces of liquid acids by pressing over porous plate. The acids, thus obtained, were perfectly solid, slightly yellowish white in colour, m. p. 52°-56°.

The mixture of the saturated acids was converted into the methyl ester (10 g.) and fractionally distilled under reduced pressure. The iodine values and the saponification values of the different fractions were determined and the mean molecular weight calculated. The M. W. of the methyl palmitate is 270·3 and that of methyl stearate 298·4. The M. W. of the three fractions lies between these two values and indicates a mixture of the two. The M. W. of the last fraction is greater than 298 and hence contains the ester of an acid of greater M. W. than stearate and probably arachidate. The percentages of the acids were determined in the different fractions by means of these mean M. W. and the iodine value (*J. Amer. Chem. Soc.*, 1920, **42**, 152).

Table IV contains the result of the fraction and Table V the results of analysis.

TABLE IV.

Fraction.	B. p.	Weight of the fraction.
1	200—210/1·2 mm.	1·6800 g.
2	278—80/0.7 mm.	3·2378
3	280—81/0·7 m.m.	2·7174
4	Residue	2·0420

TABLE VI.

Acids.	In the saturated acids.	In the original oil.
Palmitic	34·07 %	5·37 %
Stearic	61·93	9·77
Arachidic (?)	2·20	0·35
Unsaturated	1·79	0·28

TABLE V.

Fraction.	Iodine number.	Spanification value.	Mean M. W.	Unsaturated.	Mean M. W. of esters of saturated acids.
1	2·76	203·45	75·9	·0357 g. (2.12%)	275·5
2	1·69	197·74	287·2	·0423 (1·30%)	283·7
3	1·21	190·0	295·3	·0232 (0·85%)	295·3
4	4·40	186·40	301·0	·0633 (0·31%)	301·4

TABLE V (contd.).

Fraction.	Palmitic acid.	Stearic acid.	Arachidic acid.
1	1·2700 g. (75·53%)	0·2898 g. (17·25%)	...
2	1·5830 (48·9%)	1·4510 (44·82%)	...
3	0.2815 (10·36%)	2·2810 (83·93%)	...
4	...	1·6760 (82·10%)	0·2020 g. (9·89%)

Examination of the Unsaponifiable Matter.—The unsaponifiable matter obtained by ether extraction of the soap was washed in ethereal solution repeatedly with water. The dried ethereal solution was distilled when a yellowish white amorphous matter was obtained.

It was repeatedly crystallised from minimum quantity of alcohol, and thus two sets of perfectly white flakes were obtained with different melting points, and thus proving that the unsaponifiable matter is a mixture of two sterols in addition to some sticky yellow colouring matter which is practically insoluble in cold alcohol. On recrystallising from alcohol twice, the first crop melted completely at 122° with previous shrinking at 92°, and the second at 142-43° but without any sign of shrinkage before melting. They gave the various colour reactions of the sterol and were optically active, $[\alpha]_D^{32} = +16{\cdot}24$ in chloroform (c, 1·2930). The sample, crystallised from chloroform and air-dried, was analysed. [Found: C, 75·5: H, 11·1. $C_{24}H_{44}O_3$ (?) requires C, 75·8; H, 11·6 per cent]. The other sample showed $[\alpha]_D^{32} = -83{\cdot}45$ (?) in chloroform (c, 0·6890); the substance, crystallised from alcohol and air-dried, was analysed. (Found: C, 83·12, 83·41; H, 11·42, 11·66. $C_{25}H_{42}O$ requires C, 83·8; H, 11·7; while $C_{26}H_{44}O$ requires C, 83·8; H, 11·8 per cent).

SUMMARY.

The examination of the oil showed the presence of the following substances :—Oleic acid (42·93%); linolic acid (36·18%); palmitic acid (5·37%); stearic acid (9·77%); arachidic acid (?) (0·35%); and unsaponifiable matter (a mixture of two sterols, 1·2%).

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Synthesis of Coumarins and Chromones from Halogenated and Nitro-cresols.

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In view of the generalisation made by Chakravarti (*J. Indian Chem. Soc.*, 1932, **9**, 31) that the phenols which readily yield coumarins with β-ketonic esters in presence of sulphuric acid also give coumarins and not chromones in presence of phosphorus pentoxide and the phenols which give coumarins with sulphuric acid with poor yield or do not react at all, produce good yields of chromones, and in view of the influence of the halogen and nitro group on the formation of chromones (Chakravarti, *J. Indian Chem. Soc.*, 1932, **9**, 25, 31), it occurred to us that the chromone condensation (Simonis' reaction) could be facilitated by the introduction of halogen and nitro groups into the molecule of those phenols which do not satisfactorily respond to the coumarin condensation (Pechmann's reaction).

The present investigation describes the condensation of chloro- and nitrocresols (*o*-, *m*- and *p*-) with acetoacetic ester and α-alkylacetoacetic esters, both in presence of sulphuric acid and phosphorus pentoxide and the following results have been obtained:

(1) The presence of a chlorine atom in the molecule of cresol (*o*-, *m*-, and *p*-) diminishes its reactivity in Pechmann's reaction forming a coumarin and increases its reactivity in Simonis' reaction forming a chromone.

(2) The presence of a nitro group in the cresol molecule has an inhibiting influence in the coumarin condensation, but a favourable influence in chromone condensation under Simonis' conditions. Thus 4-nitro-2-methylphenol and 2-nitro-3-methylphenol do not condense with the acetoacetic esters using sulphuric acid as a condensing agent, although the chromones are easily obtained using phosphorus pentoxide.

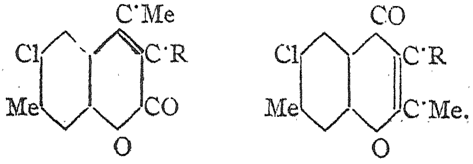
(3) The presence of an α-substituent in the acetoacetic ester molecule produces a hindrance in Pechmann's reaction, which increases with the complexity of the substituent but it has no marked influence in the chromone condensation in Simonis' reaction.

(4) The 2-methyl-group in chromones is always reactive irrespective of the position and nature of the substituents in the benzene ring (*cf.* Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2569; Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129, Cheema, Gulati and Venkataraman, *J. Chem. Soc.*, 1932, 925). The chromones, described in this paper, have been characterised by the formation of styryl derivatives by condensation with benzaldehyde in presence of alcoholic sodium ethoxide as the condensing agent. The formation of a styryl derivative serves to distinguish a 2-methylchromone from the isomeric 4-methylcoumarin.

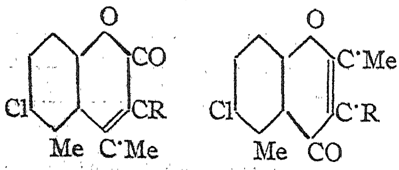
(5) The results are in full agreement with the generalisation made by Chakravarti (*loc. cit.*). If there is no formation of a coumarin or if the formation of a coumarin is slow in Pechmann's reaction, then the chromone formation is generally facilitated in Simonis' reaction.

It should be noted that Simonis' reaction is invariably attended with the formation of a considerable amount of resinous product and the isolation of the product in the purest form is always a matter of difficulty and the yield of the product in the case of the chloro- and nitro-cresols never exceeds 10-15% of the theoretical.

The coumarins and chromones, derived from 4-chloro-3-methyl phenol, may have the alternative structures (I) or (II) (R=Me, Et, Pr,



(I)



(II)

etc.) and it has not been possible to distinguish between these two structures on account of the low yields of the products.

Robertson, Waters and Jones (*J. Chem. Soc.*, 1932, 1681) detected the formation of pairs of isomeric 1:4-pyrones when Simonis' reaction was applied to *m*-cresol and methyl- and ethyl-acetoacetic esters, but in the case of chloro-*m*-cresol, however, only one product has been isolated and it has been described as (I).

EXPERIMENTAL.

The chloro-cresols *e.g.*, 4-chloro-2-methylphenol, 2-chloro-4-methylphenol, 4-chloro-3-methylphenol, have been prepared by the action of sulphuryl chloride on the cresols (Peratoner and Condorelli, *Gazzetta*, 1898, **28**, *i*, 197 ; Mezzarn and Lamberti-Zanardi, *ibid.*, 1896, **26**, *ii*, 399).

2-Nitro-3-methylphenol has been prepared according to the method of Hodgson and Beard (*J. Chem. Soc.*, 1925, **127**, 498). While preparing 2-nitro-3-methylphenol following the method of Gibson (*J. Chem. Soc.*, 1923, **123**, 1272) a yellow substance melting at 94° was obtained. On analysing it was found to be a dinitro compound, probably identical with the 2 : 6-dinitro-*m*-cresol (m.p. 99°) described by Nietzki and Ruppert (*Ber.*, 1890, **23**, 3479).

To a cold solution of *m*-cresol (21·6 c.c.) in fuming sulphuric acid (6-7% sulphur trioxide, 80 c c.) a mixture of fuming nitric acid (9·3 c.c.) and fuming sulphuric acid (6-7% sulphur trioxide, 21·3 c.c.) was slowly added with mechanical stirring, the solution being cooled in a freezing mixture. Water (100 c.c.) was added and superheated steam at 145-150° was passed. A yellow oil came over with the steam which ultimately solidified. It was filtered, m.p. 94°. (Found : N, 13·7. $C_7H_6O_5N_2$ requires N, 14·1 yer cent).

Preparation of the Coumarins.—The cresol (1 mol.) and the acetoacetic ester (1 mol.) were treated with 1½ times their weight of sulphuric acid (*d* 1·84) and the mixture kept overnight. The solution was then poured into powdered ice, when the product separated either as a solid or a thick oil, which on washing with caustic alkali solution yielded a solid. It was collected, washed with water and crystallised from acetic acid or alcohol (charcoal).

Preparation of the Chromones.—A mixture of the cresol (5 g.) and the acetoacetic ester (5 g.) was heated with phosphorus pentoxide (10 g.) on the water-bath for 1 hour. More phosphorus pentoxide (10 g.) was then added and the mixture further heated on the water-bath for 1 hour. On adding powdered ice to the reaction mixture a thick oil was generally obtained, which was extracted with ether. The ethereal solution was washed with 2*N*-caustic alkali and then with water, dried over calcium chloride and the ether removed, when crystals were obtained. The adhering oily impurity was removed on the porous plate and the product was crystallised from alcohol or acetic acid (charcoal).

Preparation of the Styryl Derivatives.—The chromone (0·2 g.-0·3 g.) was dissolved in the least quantity of absolute alcohol and the solution was treated with benzaldehyde (0·5 g.) and an alcoholic solution of sodium ethoxide (0·5 g. of sodium in 5 c.c. of absolute alcohol). After keeping overnight the solution was heated on the water-bath for ½ hour, when crystals separated from the boiling solution or on cooling or on adding a few drops of water. The crystals were collected, washed with dilute alcohol and finally crystallised from alcohol or acetic acid.

The chlorine in these compounds has been conveniently estimated by the semi-micro method (ter Meulen, *Rec. Trav. Chim.*, 1928, **47**, 698) and the nitrogen in some of the compounds has also been estimated by the semi-micro method (ter Meulen, *Rec. Trav. Chim.*, 1934, **53**, 121).

The coumarins and chromones derived from 4-chloro-2-methylphenol, 2-chloro-4-methylphenol, 4-chloro-3-methylphenol and the acetoacetic esters are described in Table I.

The chromones derived from 4-nitro-2-methylphenol, 2-nitro-3-methylphenol and the acetoacetic esters are described in Table II.

TABLE I.

Coumarins and Chromones from Chlorocresols.

Name.	Formula.	Prepared from	Condensing agent.	M. p.	Solvent from which crystallised.	Analysis. Found :	Theo :
6-Chloro-2 :8-dimethylchromone	$C_{11}H_9O_2Cl$	4-Chloro-2-methylphenol and acetoacetic ester	P_2O_5	130°	Dilute acetic acid.	Cl, 17·1%	17·0%
The *styryl* derivative	$C_{18}H_{13}O_2Cl$	—	—	176-78°	Alcohol	12·05	11·9
6-Chloro-2 : 3 : 8-trimethylchromone	$C_{12}H_{11}O_2Cl$	4-Chloro-2-methylphenol and methyl-acetoacetic ester	P_2O_5	113°	Acetic acid	15·7	15·9
The *styryl* derivative	$C_{19}H_{15}O_2Cl$	—	—	164°	Alcohol	11·3	11·4
6-Chloro-2 : 8-dimethyl-3-ethylchromone	$C_{13}H_{13}O_2Cl$	4-Chloro-2-methylphenol and ethyl-acetoacetic ester	P_2O_5	128°	Acetic acid	15·1	15·0
The *styryl* derivative	$C_{20}H_{17}O_2Cl$	—	—	154°	Alcohol	10·7	10·9
6-Chloro-2 :8-dimethyl-3-propylchromone	$C_{14}H_{15}O_2Cl$	4-Chloro-2-methylphenol and propyl-acetoacetic ester	P_2O_5	120°	Acetic acid	13·6	14·1
The *styryl* derivative	$C_{21}H_{19}O_2Cl$	—	—	135°	Alcohol	10·3	10·4
8-Chloro-4 :6-dimethylcoumarin	$C_{11}H_9O_2Cl$	2-Chloro-4-methylphenol and acetoacetic ester	H_2SO_4	105°	Acetic acid	17·1	17·04
8-Chloro-3 :4 :6-trimethylcoumarin	$C_{12}H_{11}O_2Cl$	2-Chloro-4-methylphenol and methyl-acetoacetic ester	H_2SO_4	152°	Acetic acid	16·0	15·9

TABLE I (contd.).

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Solvent for crystallisation.	Analysis	
						Found :	Theo :
8-Chloro-2 : 3 :6-trimethylchromone	$C_{12}H_{11}O_2Cl$	2-Chloro-4-methylphenol and methyl-acetoacetic ester	P_2O_5	150°	Acetic acid	Cl, 16·0%	Cl, 15·9%
The *styryl* derivative	$C_{19}H_{15}O_2Cl$	—	—	183°	Alcohol	11·54	11·4
8-Chloro-4 : 6-dimethyl-3-ethylcoumarin	$C_{13}H_{13}O_2Cl$	2-Chloro-4-methylphenol and ethyl-acetoacetic ester	H_2SO_4	146°	Acetic acid	14·8	15·0
8-Chloro-2 :6-dimethyl-3-ethyl-chromone	$C_{13}H_{13}O_2Cl$	,,	P_2O_5	105°	Acetic acid	14·7	15·0
The *styryl* derivative	$C_{20}H_{17}O_2Cl$	—	—	132°	Alcohol	10·7	10·9
3 :8-Dichloro-4 :6-dimethylcoumarin	$C_{11}H_8O_2Cl_2$	2-Chloro-4-methylphenol and α-chloro-acetoacetic ester	H_2SO_4	110°	Alcohol	28·8	29·1
6-Chloro-4 :7-dimethylcoumarin	$C_{11}H_9O_2Cl$	4-Chloro-3-methylphenol and acetoacetic ester	H_2SO_4	208°	Acetic acid	17·5	17·03
6-Chloro-3 :4 :7-trimethylcoumarin	$C_{12}H_{11}O_2Cl$	4-Chloro-3-methylphenol and methyl-acetoacetic ester	H_2SO_4	146°	Acetic acid	16·6	15·9
6-Chloro-2 :3 :7-trimethylchromone	$C_{12}H_{11}O_2Cl$	4-Chloro-3-methylphenol and methyl-acetoacetic ester	P_2O_5	94°	Acetic acid	15·9	15·9
The *styryl* derivative	$C_{19}H_{15}O_2Cl$	—	—	153°	Alcohol	11·6	11·4
6-Chloro-3-ethyl-4 :7-dimethyl-coumarin	$C_{13}H_{13}O_2Cl$	4-Chloro-3-methylphenol and ethyl-acetoacetic ester	H_2SO_4	136°	Acetic acid	14·8	15·0

TABLE I (contd.).

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Solvent for crystallisation.	Analysis	
						Found :	Theo :
6-Chloro-3-ethyl-2 :7-dimethylchromone	$C_{13}H_{13}O_2Cl$	4-Chloro-3-methylphenol and ethyl-acetoacetic ester	P_2O_5	113°	Acetic acid	Cl, 15·1%	Cl, 15·0%
The *styryl* derivative	$C_{20}H_{17}O_2Cl$	—	—	155°	Alcohol	11·0	10·9
6-Chloro-3-propyl-2 :7-dimethylchromone	$C_{14}H_{15}O_2Cl$	4-Chloro-3-methylphenol and propyl-acetoacetic ester.	P_2O_5	92°	Acetic acid	14·0	14·1
The *styryl* derivative	$C_{21}H_{19}O_2Cl$	—	—		Alcohol	10·5	10·4
6-Chloro-7-methyl-coumarin-4-acetic acid	$C_{12}H_9O_4Cl$	4-Chloro-3-methylphenol and acetone dicarboxylic acid	H_2SO_4	185-88°	Acetic acid	13·6	14·05
3 :6-Dichloro-4 :7-dimethylcoumarin	$C_{11}H_8O_2Cl_2$	4-Chloro-3-methylphenol and α-chloro-acetoacetic ester	H_2SO_4	210°	Acetic acid	29·5	29·1
6-Chloro-4 :7-dimethyl-coumarin-3-acetic ester	$C_{15}H_{15}O_4Cl$	4-Chloro-3-methylphenol and ethyl aceto-succinate	H_2SO_4	110-12°	Acetic acid	12·08	12·1

TABLE II.

Chromones from Nitrocresols.

6-Nitro-2 :3 :8-trimethylchromone	$C_{12}H_{11}O_4N$	4-Nitro-2-methylphenol and methyl-acetoacetic ester	P_2O_5	245°	Acetic acid	N, 5·8%	N, 6·0%
The *styryl* derivative	$C_{19}H_{15}O_4N$	—	—	225°	Alcohol	4·2	4·3
6Nitro-2 :8-dimethyl-3-ethylchromone	$C_{13}H_{13}O_4N$	4-Nitro-2-methylphenol and ethyl-acetoacetic ester	P_2O_5	233°	Acetic acid	5·9	5·6
The *styryl* derivative	$C_{20}H_{17}O_4N$	—	—	205°	Alcohol	3·9	4·1

TABLE II (contd.).

Chromones from Nitrocresols.

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Solvent for crystallisation.	Analysis Found :	Theo :
6-Nitro-2 :8-dimethyl-3-propyl-chromone	$C_{14}H_{15}O_4N$	4-Nitro-2-methylphenol and propyl-acetoacetic ester	P_2O_5	200°	Acetic acid	N, 5·27%	N, 5·30%
8-Nitro-2 :7-dimethyl-3-chromone	$C_{11}H_9O_4N$	2-Nitro-3-methylphenol and acetoacetic ester	P_2O_5	130°	Alcohol	6·2	6·30
8-Nitro-2 :7-dimethyl-3-ethylchromone	$C_{13}H_{13}O_4N$	2-Nitro-3-methylphenol and ethyl-acetoacetic ester	P_2O_5	137°	Alcohol	5·1	5·60

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The Enzymes in Snake Venom. Part. II. Their Action on Native Proteins, on Peptone and on the Activity of Trypsin.

By B. N. Ghosh and S. S. De.

It has been recorded by several authors, as early as 1902-1903 that snake venom contains proteolytic enzymes. The behaviour of these enzymes has not yet been fully investigated. Recently Masakazu Sato and Tamatsu Hirano (*Mem. Facult. Sci. Agric. Taihoku*, 1935, **9**, 83) have found that the venoms of some Formosan snakes can digest proteins and that their optimum activity lies between p_H 8·0 to p_H 8·5 depending on the nature of the substrate used.

In a previous paper it has been shown by one of us (Ghosh, *J. Indian Chem. Soc.*, 1936, **13**, 450), that the proteolytic enzyme in cobra (*Naja Naja*) venom resembles trypsin so far as its activity depends on the p_H of the substrate suspension. Since *Vipera Russelli* belongs to a group quite different from that of cobra, a study of the enzymes in its venom was undertaken.

EXPERIMENTAL.

Action of Russell's Viper Venom on Proteins.

The experimental procedure adopted was the same as described by Ghosh (*loc. cit.*) in a previous paper. Stock solutions (5%) of gelatin (electro-dialysed), Merck's dried egg-albumin and of casein were prepared and kept in a refrigerator with a few drops of toluene as preservative.

Solution of Russell's viper venom (1%) in 0·85% NaCl solution was prepared and its toxicity determined. It was found that 0·01 mg. of venom (dry weight) kills a pigeon weighing 300 g. when injected intravenously.

The stock protein solution (20 c.c.) was taken in an Erlenmeyer's flask and its p_H adjusted to the requisite value by adding a few drops of HCl or NaOH according to need. To this solution 10 c.c. of buffer solution of the same p_H were added. 10 C.c. of this buffered protein solution were placed in each of the two conical flasks. To one of the flasks, 2 c.c. of the venom solution and 8 c.c. of physiological saline were added. To the other, which served as control, 10 c.c. of physiological saline only were added. After adding a few drops of toluene to each of the flasks, they were stoppered and placed in a thermostat at 36°. After suitable intervals of time, 5 c.c. portions of the solution were withdrawn from each set of flasks and added to 45 c.c. of absolute alcohol to which 0·5 c.c. of 0·5% thymolphthalein solution in alcohol was previously added. To the flask containing the 5 c.c. control sample, 0·5 c.c. of the venom solution were added just before titration. The interval of time allowed for digestion was 24 hours. The buffer solutions used are acid potassium phthalate from p_H 2·2 to p_H 5·8, acid potassium phosphate from p_H 6·0 to p_H 8·0 and boric acid and potassium chloride from p_H 8·2 to p_H 10. The results are recorded in Tables I—III.

TABLE I.

Substrate—Egg-albumin. Venom—Russell's viper.

0·0456 *N* alcoholic KOH required in c.c. for titration of 5 c.c. of the soln.

p_H.	Active venom and substrate.	Control.	Diff.	p_H.	Active venom and substrate.	Control.	Diff.
2·4	4·9	4·9	0·0	7·6	2·44	2·06	0·38
3·6	4·35	4·35	0·0	8·0	2·14	1·72	0·42
5·0	2·70	2·65	0·65	8·6	1·74	1·40	0·34
6·0	3·27	3·15	0·12	9·0	1·32	1·10	0·22
6·6	2·86	2·70	0·16	9·4	0·92	0·8	20·1
7·0	2·66	2·42	0·24				

TABLE II.

Substrate—Casein. Venom—Russell's viper.

0·0456 *N*-alcoholic KOH required in c.c. for titrating 5 c.c. of the soln.

p_H.	Active venom and substrate.	Control	Diff.	p_H,	Active venom and substrate.	Control.	Diff.
5·0	3·04	2·92	0·12	7·6	2·95	2.35	0·60
6·0	4·09	3·74	0·35	8·0	2·21	1·70	0·51
6·6	3·76	3·22	0·54	8·6	1·74	1·35	0·39
7·0	3·38	2·76	0·62	9·0	1·24	0·95	0·29

TABLE III.

Substance—Gelatin. Venom—Russell's viper.

0·0456 *N*-alcoholic KOH required in c.c. for titrating 5 c.c. of soln.

p_H.	Active venom and substrate.	Control.	Diff.	p_H.	Active venom and substrate.	Control.	Diff.
5·0	1·75	1·64	0·11	8·0	1·60	1·12	0·48
6·0	2·24	2·06	0·18	8·6	1·42	0·98	0·44
6·6	2·01	1·76	0·25	9·0	1·24	0·90	0·34
7·0	1·85	1·54	0·31	9·4	0·98	0·78	0·20
7.6	1·75	1·30	0·45				

It will be noticed from the data recorded in the Tables I—III that the optimum activity of the protease in Russell's viper venom using gelatin and egg-albumin as substrates is at p_H 8·0 approximately, while with a casein suspension it is in the neighbourhood of p_H 7·0. The proteolytic enzymes in the venoms of cobra and Russell's viper thus resemble trypsin in so far as their activity depends on the p_H of the substrate suspension.

Action of the Venoms of Cobra and Russell's Viper on Peptone.

It has been recorded by Launey (*Compt. rend.*, 1902, **135**, 401) that the disintegration of proteins like casein and serum albumin by the action of venoms of cobra and of the viper proceeds so far as to the stage of albumose. It never leads to the formation of peptone. It is not yet known whether the venoms of cobra or of Russell's viper can hydrolyse peptone to simpler compounds. The action of these venoms on solutious of Witte's peptone at different p_H was, therefore, investigated. The experimental procedure was the same as described before. The results are given in Tables IV and V.

TABLE IV.

Substrate—peptone. Venom—cobra.

0·0403 *N*-EtOH-KOH required for titrating 5 c.c. of the soln.

p_H.	Active venom and substrate.	Control.	Diff.
6·0	5·94	5·54	0·40
6·6	5·14	4·68	0·46
7·0	4·62	4·08	0·54
7·6	3·78	3·12	0·66
8·0	3·26	2·56	0·70
8·6	2·67	1·95	0·72
9·0	2·20	1·52	0·68
9·4	1·80	1·24	0·56

TABLE V.

Substrate—peptone. Venom—Russell's viper.

0·0449 *N*-EtOH-KOH required for titrating 5 c.c. of soln.

p_H.	Active venom and substrate.	Control.	Diff.
6·0	5·77	5·52	0·25
6·6	4·96	4·66	0·30
7·0	4·44	4·08	0·36
7·6	3·56	3·10	0·46
8·0	3·05	2·55	0·50
8·6	2·47	1·94	0·53
9·0	1·98	1·50	0·48
9·4	1·65	1·25	0·40

From an examination of the data in the Tables IV and V it appears that both the venoms can disintegrate Witte's peptone. For the same weight, the activity of cobra venom is greater than that of Russell's viper venom. The optimum activity of the peptidase in both the venoms is in the region of p_H 8·2 to p_H 8·5. This shows that the venoms contain an enzyme identical with or similar to erepsin.

Action of Snake Venom on the Activity of Trypsin.

Delezenne (*Compt. rend.*, 1902, **135**, 329) studied the effect of snake venom on the proteolytic activity of pancreatic juice. It was found that although snake venom alone cannot digest egg-albumin coagulated by heat yet when it was added to inert pancreatic juice it led to the rapid digestion of the coagulated protein. On heating, to 100° for 15 minutes, it was found to have lost its power of activating the inert pancreatic juice. Delezenne (*loc. cit.*) therefore concluded that snake venom contains a kinase similar to enterokinase. Recently Delezenne's observation has been confirmed by Masakazu Stato and Tamotsu Hiyono (*Mem. Facult. Sci. Agric. Taihoku*, 1935, **9**, 105), who used glycerol extract of pancreas instead of inactive pancreatic juice. In our experiments we tried the effect of venoms of cobra and Russell's viper on the activity of trypsin (Merck) to find out if they contain some trypsin activator. The experimental procedure adopted was the same as described already. Sets of flasks containing substrate only, substrate and 1 c.c. of 0·1% trypsin, substrate and 2 c.c. of 1% venom, and substrate, trypsin and venom, were placed in a thermostat at 36°. The final volume of the mixtures in each of the flasks was 20 c.c. and the concentration of the substrate was the same in all the flasks. The data are recorded below.

TABLE VI.

Venom—Russell's viper. Substrate—gelatin. Time—after 6 hours' incubation.

0·0448 *N*-EtOH-KOH required for titrating 5 c c. of soln.

p_H.	Control.	Venom.	Trypsin.	Trypsin and venom.	Diff. between Columns 3 and 4.
6·0	2·08	2·13	3·04	2·2	0·84
7·0	1·58	1·65	2·94	1·74	1·20
7·6	1·32	1·44	2·84	1·52	1·32
8·5	1·02	1·12	2·28	1·22	1·06

TABLE VII.

Venom and substrate—same as in Table VI. Time—after 24 hours' incubation.

0 0448 *N*-EtOH-KOH required for titrating 5 c.c. of the soln

p_H.	Control.	Venom.	Trypsin.	Trypsin and venom.	Diff. between columns 3 and 4.
6·0	2·10	2·30	3·95	2·52	1·43
7·0	1.58	1·90	4·10	2.40	1·70
7·6	1.34	1·78	4·04	2·24	1·80
8·5	1·00	1·42	3·46	1·76	1·70

TABLE VIII.

Venom—cobra. Substrate—gelatin. Time—after 24 hours' incubation.

0·0441 *N*-EtOH-KOH required for titrating 5 c.c. of the soln.

p_H.	Control.	Venom.	Trypsin.	Trypsin and venom.	Diff. between columns 3 & 4.
6·0	2·28	2·56	3·94	3·00	0·94
7·0	1·70	2·18	4·03	2·82	1·21
7·6	1·45	2·00	3·95	2·75	1·20
8·5	1·10	1·62	3·42	2·35	1·07

TABLE IX.

Venom—Russell's viper. Substrate—peptone (Witte). Time 24 hours' incubation.

0·0422 *N*-EtOH-KOH required for titrating 5 c.c. of the soln.

p_H	Control.	Venom.	Trypsin.	Trypsin and venom.	Diff. between columns 3 & 4.
6·0	5·06	5·26	6·38	5·71	0·67
7·0	3·72	4·04	5·73	4·94	0·79
7·6	2·85	3·25	5·11	4·30	0·81
8·5	1·85	2·33	4·15	3·41	0·74

It is evident from the data recorded above that the venoms used contain a trypsin inhibitor. It may be mentioned here that the activation of inert pancreatic juice by snake venom as observed by Delezenne (*loc. cit.*) can be accounted for without assuming the existence of enterokinase in the venom. Recently Northrop and co-workers (U. N. Science, 1933, 78) have shown that in pancreatic extract there is another proteolytic enzyme besides trypsinogen and this they termed chymotrypsinogen. They further showed that a trace of trypsin can convert inactive chymotrypsinogen to the active form chymotrypsin. Addition of snake venom, which we have already shown contains trypsin, to the inactive pancreatic juice will convert chymotrypsinogen to the active form chymotrypsin. This would account for the increased proteolytic activity of the pancreatic juice as observed by Delezenne (*loc. cit.*) and Masakatsu Sato (*loc. cit.*).

SUMMARY.

1. The optimum activity of the proteolytic enzyme in Russell's viper venom is at about p_H 8·0 using gelatin and egg-albumin as substrates, while with casein as substrate it is in the neighbourhood of p_H 7·0. The protease in Russell's viper venom thus resembles trypsin.

2. The venom of cobra and of Russell's viper can digest Witte's peptone. The optimum activity of the peptidase contained in these venoms lies between p_H 8·2 to p_H 8·4. The peptidase in these venoms is therefore similar to erepsin.

3. The addition of cobra or of Russell's viper venom to trypsin (Merck) inhibits its proteolytic activity to a marked extent. These venoms, therefore, contain some trypsin inhibitor.

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Constituents of the Leaves of *Vitex Negundo*.

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Vitex negundo, Linn., Vern. *Nishinda* (Beng.) *Samhalu* (Hindi), is common throughout India. Various medicinal properties are ascribed to the leaves and the roots of this plant in the Indian system of medicines. The leaves are said to be vermifuge and a tonic. The decoction of the leaves is given in catarrhal fever and the juice is used for removing foetid discharges and worms from ulcers (Kirtikar and Basu, "Indian Medicinal Plants" II, p. 999). Nothing was known about the constituents of the leaves to account for these medicinal properties, excepting that Broosma (Wehmer, "Planzen Stoffe" p. 647) has found a trace of an alkaloid in the leaves. It was, therefore, thought desirable to examine the constituents of the leaves in detail with a view to find out the active principles.

The mature leaves of the plant, collected in September and October, were first examined and an amorphous basic substance of an alkaloidable nature (0·03%) could be isolated. Since the amount present was very small, it was not examined further. From the alcoholic extract a crystalline substance was obtained, which from its analysis and other properties appears to be gluco-nonitol. Occurrence of gluco-nonitol, a synthetic product so far, in nature is a matter of considerable interest. Besides fatty and resinous matter, nothing crystalline could be isolated from the water-soluble portion of the alcoholic extract; but in the water-insoluble portion three crystalline acids were found to be present: the one, occurring in the largest amount (0·3%) on the leaves is *p*-hydroxybenzoic acid; the second acid appears to be 5-oxy-*iso*phthalic acid and the third acid has been identified as 3:4-dioxybenzoic acid. Besides the above crystalline acids a fair amount of tannic acid is also present. From the basic lead acetate precipitate, an amorphous glucoside has been isolated, which is very soluble in water and yields *p*-hydroxybenzoic acid, glucose and a dark brown amorphous substance on hydrolysis with hot acids or with sodium ethylate. Examination of the fresh flush of leaves, collected in February and March, revealed the presence of a different micro-crystalline glucoside, sparingly soluble in cold water and dilute mineral acids (about 2%), or even by boiling with water alone, it breaks up into *p*-hydroxybenzoic acid, glucose and a dark brown (almost black) amorphous substance. Hydrolysis with ice-cold alcoholic sulphuric acid (5%), however, yields glucose and two amorphous substances, one of them being acidic and the other neutral in reaction. Both of these hydrolysis products, on being boiled with sulphuric acid (2%) yields *p*-hydroxybenzoic acid and the same dark brown amorphous substance, as in the case of the original glucoside. Hydrolysis with alcoholic potash, on the other hand, yields *p*-hydroxybenzoic acid and a second crystalline glucoside, which on further hydrolysis with cold dilute sulphuric acid (5% alcoholic) breaks up into glucose and a yellow brown amorphous substance. Further work to elucidate the composition of this substance is in hand. Tentatively the formula $C_{20}H_{24}O_{11}$ is being given to the original glucoside and $C_{13}H_{20}O_9$ to the second glucoside, which is its alkali hydrolysis product. Thus the two glucosides, one isolated from mature leaves and the other from the fresh flush of leaves, although they differ considerably in their properties, appear to be closely related in so far that both on hot acid hydrolysis yield *p*-hydroxybenzoic acid, glucose and a dark brown amorphous substance.

As regards the physiological properties of the leaves, their germicidal action appears to be due to the presence of *p*-hydroxybenzoic acid. The glucoside has been sent to the Department of Pharmacology, School of Tropical Medicine, Calcutta, for determination of its physiological properties. Preliminary examination has shown it to be physiologically active. A detailed report will be published in due course.

EXPERIMENTAL

Mature Leaves Collected in September and October.

Extraction of the Leaves with Alcohol.—Several kg. of the powdered leaves were extracted by percolation with cold alcohol (90-94%). Bulk of the alcohol was removed by distillation under reduced pressure and the concentrated extract allowed to stand for 3-4 days, when some crystals (I) separated. From the filtrate, alcohol was removed completely and the residue was extracted with hot water. The insoluble matter, which contained fatty and resinous matter, was examined further, but nothing crystalline was obtained. The filtered aqueous extract was concentrated to a syrup under reduced pressure and repeatedly extracted with ether. The ether extract was concentrated and repeatedly extracted with small quantities of sodium carbonate solution. On removal of the ether a small quantity of a brown resinous substance remained which was not examined further.

The dark yellow sodium carbonate solution was acidified with sulphuric acid, saturated with common salt and repeatedly extracted with ether. On removal of the ether, the free acids (II) came out as a dark brown crystalline mass.

The concentrated aqueous solution, after being extracted with ether, was diluted to thrice its volume and lead acetate solution was added when a deep yellow precipitate (III) was obtained. To the filtrate and washing basic lead acetate was added, when a canary yellow precipitate (IV) was obtained. The filtrate was freed from lead and examined but nothing crystalline was obtained. It only gave reactions of sugar.

Gluco-nonitol.—The crystalline substance (I) was found to be readily soluble in water but practically insoluble in absolute alcohol. It was recrystallised thrice from dilute alcohol when it came out as perfect white needles, m.p. 196-98°. It does not reduce Fehling's solution. It is very slightly dextro-rotatory, $[\alpha]^{20}_{D} = +1{\cdot}5°$; (6·6% aqueous solution). (Found : C, 39·9 ; H 7·5. $C_9H_{20}O_9$ requires C, 39·7 ; H, 7·4 per cent).

The *acetyl* derivative, prepared with acetic anhydride and freshly fused zinc chloride, crystallised from ethyl acetate and finally from absolute alcohol, m.p. 179-80°, yield 3·2 g. from 2·5 g. [Found: C, 49·9; H, 6·2. $C_9H_{11}O_9\ (CH_3\ CO)_9$ requires C, 49·8; H, 5·8 per cent]. On saponification with caustic potash 0·5280 g. of the substance gave 0·430 g. of acetic acid *i.e.*, 81% on the weight of the substance. $C_9H_{11}O_9\ (CH_3\ CO)_9$ should yield 83% of its weight of acetic acid.

Lead acetate precipitate (III).—It was decomposed with sulphuretted hydrogen. Lead and H_2S were removed and the aqueous solution was concentrated to a small bulk under reduced pressure, and then extracted repeatedly with ether. The ethereal solution was extracted several times with sodium carbonate solution and the latter acidified and again extracted with ether, the ether was removed, when a crystalline magma (III*a*) was obtained. The concentrated aqueous solution after extraction with ether, was examined but nothing besides tannic acid could be detected.

Free Acids.—The crystalline acidic substance (II) crystallised from hot water as prismatic needles, m.p. 208-9°. These crystals gave greenish blue colour with ferric chloride, a precipitate with lead acetate and a copious light yellow precipitate with basic lead acetate. The mother liquor also gave a deep greenish blue colour with ferric chloride and a precipitate with lead acetate. The crystalline magma (III*a*) also behaved in the same way, The two crystalline magmas (II) and (III*a*) were, therefore, combined, dissolved in boiling water and filtered from insoluble resins. The clear solution was then treated with lead acetate The light yellow precipitate (III*b*) was removed and examined separately The filtrate was deleaded and evaporated to a small bulk when stout prismatic needles, m.p. 210-11°, were obtained, which when recrystallised from water (charcoal) melted at 215-16°.

The properties and analysis showed that it is probably *p*-hydroxybenzoic acid, and this was confirmed by preparation of the ethyl ester (m.p. 115-16°), the *methoxy* derivative (m p. 181-82°, mixed m.p,) and tribromophenol (m.p. 93-94°, mixed m.p.) (Found : C, 60·86; H, 4·75. Calc. for $C_7H_6O_3$: C, 60·87; H, 4·35 per cent).

5-*Oxy*-iso*phthalic Acid.*—The lead acetate precipitate (III*b*) was suspended in water and decomposed with sulphuretted hydrogen. On removal of sulphuretted hydrogen and concentration on water-bath crystals separated which were recrystallised from hot water, m.p. 285-87°. The substance was very sparingly soluble in cold water, readily soluble in boiling water, alcohol and ether. It gave a yellow brown colour with ferric chloride and white precipitate with lead acetate and silver nitrate. It sublimed and heated with lime it gave off phenol. It appears that this acid is 5-oxy-*iso*phthalic acid (m.p. 288°). The quantity isolated, however, was too small for definite characterisation.

3:4-*Dioxybenzoic Acid.*—After removal of the above acid and concentration of the mother-liquor almost to a syrup and allowing it to stand for some days a crystalline magma was obtained, which was drained on porous plate and recrystallised from benzene and alcohol. Recrystallised from a very small quantity of water it was obtained as faintly yellow needles, m.p. 197-98°.

The analysis and properties all agree with 3:4-dioxy-benzoic acid. (Found: C, 54·8; H, 3·7. Calc. for $C_7H_6O_4$: C, 54·5; H, 3·7 per cent).

Amorphous Glucoside.—The basic lead acetate precipitate (IV) was decomposed with sulphuretted hydrogen. The filtrate, after removal of lead and H_2S, was made just neutral, concentrated to a small bulk under reduced pressure, acidified and extracted with ether. which removed some *p*-hydroxybenzoic acid. The aqueous solution was neutralised and further concentrated to a thick syrup under reduced pressure. It was then absorbed in filter paper, dried and extracted in a Soxhlet with methyl alcohol, the extract was concentrated, but no crystals separated. It was then poured on to acetone, filtered and the yellow solution decolourised, the solvent removed and the residue dried. A light brown amorphous substance was obtained (0·74 % on leaves) which was very soluble in water and alcohol, less soluble in acetone and ethyl acetate and insoluble in ether, chloroform and petroleum ether. It was purified by solution in alcohol and precipitation by ether, m.p. 93-95°. It did not reduce Fehling's solution but did so after hydrolysis with dilute sulphuric acid. The pure glucoside did not give any precipitate with lead acetate nor any colour with ferric chloride.

On hydrolysis with sulphuric acid (5%) on a water-bath for 6 hours, a dark brown amorphous substance separated. It was extracted with ether, which did not dissolve the dark brown substance. From the ether extract crystals were obtained which recrystallised from water (m. p. 215-16°) and was proved to be *p*-hydroxybenzoic acid. The acidic solution, after removal of the dark brown substance and *p*-hydroxybenzoic acid, was found to contain only glucose (phenylosazone, m.p. 208°).

2·3 G. of the glucoside was dissolved in methyl alcohol (10 c.c.) and sodium (0·2 g.) dissolved in methyl alcohol (10 c.c.) was added and the whole heated on a water-bath for 3 hours. Alcohol was removed and the residue dissolved in water, the clear reddish brown solution was acidified with sulphuric acid and extracted with ether, the ether removed and *p*-hydroxybenzoic acid was obtained. From the solution after extraction with ether, nothing excepting glucose could be detected.

Fresh Flush of Leaves Collected in February and March.

Alcoholic Extract of the Leaves.—As before the air-dried leaves were extracted with alcohol by cold percolation. From the concentrated alcoholic extract crystals of gluco-nonitol were removed and the filtrate was freed from alcohol. The residue was extracted with boiling water, filtered and allowed to stand overnight. A voluminous greenish-blue crystalline magma separated. This was never noticed before in the case of mature leaves. The substance was sparingly soluble in cold water, fairly soluble in hot water and in 90% alcohol and insoluble in ether and chloroform. Preliminary examination showed it to be a glucoside. After removal of this glucoside, the filtrate was examined for free acids; only *p*-hydroxybenzoic acid and 3:4-dioxybenzoic acid were found to be present.

The Glucoside present in the Fresh Flush of Leaves.—The crude glucoside was purified by solution in pyridine and fractional precipitation with chloroform, yield 2·2% on the leaves, m.p. 152-53° (decomp.). It was further purified by solution in alcohol and fractional precipitation with ether ; a yellow-brown colouring matter was first precipitated and then the glucoside. Repeating the operation thrice an almost colourless microcrystalline substance was obtained, m. p. 154-55°; $[\alpha]_D^{20} = -92{\cdot}6°$ (3·23% absolute alcoholic solution). It is neutral in reaction and is very sensitive to heat and mineral acids. Heated with dilute mineral acids and even with acetic acid it breaks up into *p*-hydroxybenzoic acid, sugar and a dark brown (almost black) amorphous substance, which is insoluble in water, only partly so in alcohol or acetone and insoluble in most organic solvents. Even at ordinary temperature (25°) dilute mineral acids slowly decompose the glucoside into the above substances. It is similarly decomposed by prolonged boiling with water. It does not give any precipitate with lead acetate but gives a copious white precipitate with basic lead acetate. It gives a reddish violet colour with ferric chloride.

Acid Hydrolysis of the Glucoside.—The glucoside (5 g.) in alcohol (50 c.c.) was cooled in ice, and ice-cold sulphuric acid (2·5 c.c. in 10 c.c. water, 10 c.c.) added and the mixture kept in a thermoflask in ice for 7 days. The green solution was poured on to ether, ether decanted off and the aqueous layer was washed with ether thrice. The combined ethereal solution was extracted repeatedly with sodium carbonate solution, the ether removed when a viscous, light brown substance (A) (about 24% of the glucoside) was obtained. From the ice-cold alkali solution, acidified with sulphuric acid, ether extracted an acidic substance (B) which was also amorphous and varnish-like (about 34% of the glucoside). The original green aqueous acid solution was found to contain only sugar (about 42%) (phenylosazone, m.p. 208-9°).

The neutral substance (A) was purified by solution in ether and pouring into petroleum ether. All attempts to crystallise the light brown viscous precipitate failed. Further hydrolysis by boiling with dilute sulphuric acid resulted in the formation of the dark brown amorphous substance and *p*-hydroxybenzoic acid. No sugar was present. The acidic substance (B) was purified in the same way. It was also an amorphous substance of light brown colour which would not crystallise. Hydrolysed with alcoholic sulphuric acid (5%) on a water-bath for 4 hours it gave *p*-hydroxybenzoic acid (35% of its weight) and the same dark brown substance. Hydrolysed with sodium ethylate in alcoholic solution, it also gave *p*-hydroxybenzoic acid (34·4%) and a dark yellow-brown neutral substance which would not crystallise. This neutral substance readily absorbed bromine and gave a crystalline bromo compound insoluble in cold water, readily soluble in alcohol and ether. Recrystallised from ether it was obtained as long needles, m.p. 92-93°. Further work is in progress to determine the nature of this substance.

Alkali Hydrolysis of the Glucoside.—The purified glucoside (10 g.) was hydrolysed with alcoholic potash (100 c.c., 5%) on a water-bath for 6 hours. Alcohol was removed and the residue dissolved in a small quantity of water, cooled in ice, acidified and extracted with ether. On removal of ether *p*-hydroxybenzoic acid was obtained. The aqueous solution was neutralised and evaporated to dryness and the residue was extracted in a Soxhlet with alcohol, the alcoholic extract, decolourised and bulk of the alcohol removed and a little ether added till slightly opalescent crystalline needles came out. These were recrystallised from ether-alcohol, m.p. 173-74°. It is readily soluble in cold water. It does not give any precipitate with either, lead acetate or basic lead acetate and no colour with ferric chloride. On being further hydrolysed by dilute sulphuric acid, it gives a dark brown amorphous substance and glucose but no *p*-hydroxybenzoic acid. It has $[\alpha]^{20°}_{D} = -163·6°$ (5·136% aqueous solution) and M.W., 310. It is, therefore, a second glucoside formed from the original glucoside by the splitting off of *p*-hydroxybenzoic acid from its molecule by alkali. The glucose content of this substance, as estimated by Fehling's solution, is about 58%. Further hydrolysis of this product with alcoholic sulphuric acid (5%) at about 12° for 24 hours gave glucose and a deep yellow-brown amorphous substance, neutral in reaction, insoluble in water, but readily soluble in ether and alcohol. The nature of this substance is being investigated.

The original glucoside was found to contain about 42% of glucose (Found: C, 54·9; H, 5·6; M. W., 429. $C_{20}H_{24}O_{11}$ requires C, 54·5; H, 5·5 per cent. M. W., 440). The second glucoside should, therefore, have a formula $C_{13}H_{20}O_{9}$. (Found: C, 48·7; H, 5·8. $C_{13}H_{20}O_{9}$ requires C, 48·8; H, 6·2 per cent). The molecular weight, as found from its sugar content, is also in close agreement.

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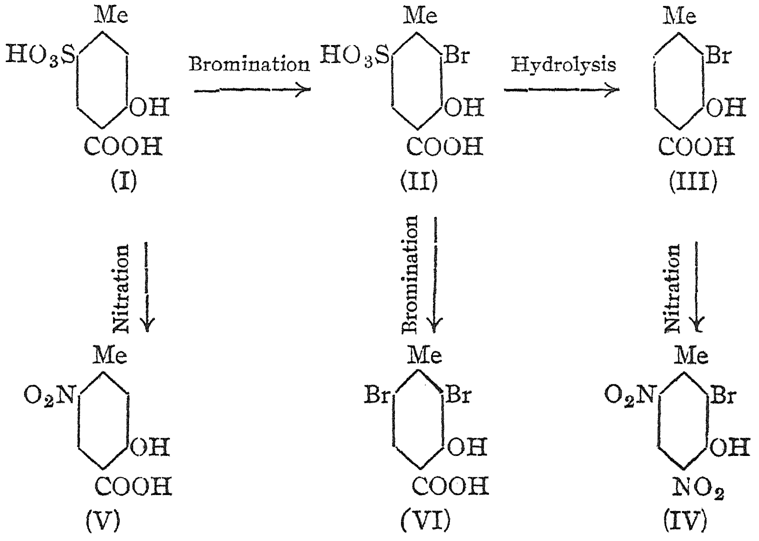
6-Sulpho-*m*-cresotic Acid and Related Compounds.

By (Late) A. N. Meldrum and C. N. Bamji.

In view of the fact that 6-chlorocresotic acid is a more powerful antiseptic than the 5-chloro compound, 6-sulphocresotic acid (I) has been prepared by the sulphonation of *m*-cresotic acid. The constitution (I) follows from its conversion to (II) by bromination and the subsequent hydrolysis of (II) into (III).



(III) on nitration gave (IV) identical with 4:6-dinitro-2-bromo-*m*-cresol (Gibbs and Robertson, *J. Chem. Soc.*, 1914, **105**, 1886). The compounds (V) and (VI), prepared as indicated on the diagramatic scheme, also support the constitution (I) of sulpho acid. The bromocresotic acid of Gattermann (*Ber.*, 1893, **26**, 1851), which he prepared from a nitro-*m*-cresotic acid, is identical with the above acid and hence it is 2-bromo-*m*-cresotic acid and not the 6-bromo-acid as was supposed by him. Walther and Zipper's bromo acid, m.p. 221°, (*J pr. Chem.*, 1915, *ii*, **91**, 364) is different from Gattermann's acid.

When brominated in acetic acid (II) gives (VI) by extrusion of the sulphonic group. In dilute acetic acid solution, the carboxy group even is eliminated resulting in tribromo-*m*-cresol. Use of 20% hydrobromic acid avoids these extrusions of groups.

Nitration of (I) with dilute nitric acid at 60° or in acetic acid at 30° gives 6-nitro-*m*-cresotic acid (Einhorn, *Annalen*, 1900, **311**, 477) and in sulphuric acid with a mixture of nitric and sulphuric acids, dinitro *m*-cresotic acid is obtained, while the sulponitro-*m*-cresotic acid is obtained only when nitration is carried out in fuming sulphuric acid with a mixture of fuming nitric and sulphuric acids.

EXPERIMENTAL.

*6-Sulpho-*m*-cresotic Acid.*—*m*-Cresotic acid (40 g.) was slowly dissolved at room temperature in sulphuric acid (60 c.c., 100%). The sulphonic acid separated completely in about 24 hours. It crystallised from water either in needles or plates, m.p. 93°. (Found: Equiv., 152·0. $C_8H_8O_6S, 4H_2O$ requires Equiv., 152·1).

The *Acid Potassium Salt* crystallised from water in white slender needles. (Found: K, 12·1; H_2O, 16·4; Equiv., 322·0. $C_8H_7O_6SK, 3H_2O$ requires K, 12·0 ; H_2O, 16·7 per cent. Equiv., 324·3).

The *Acid Sodium Salt* crystallised in slender needles from water. (Found: Na, 8·6; H_2O, 6·7; Equiv., 272·8. $C_8H_7O_6SNa, H_2O$ requires Na, 8·5 ; H_2O, 6·6 per cent. Equiv., 272·1).

The *Acid Calcium Salt* crystallised from water in small needles. [Found: Ca, 6·3 ; Equiv., 292·9. $(C_8H_7O_6S)_2$ Ca, $5H_2O$ requires Ca, 6·7 per cent. Equiv., 296·1].

The *Acid Barium Salt* crystallises from water. [Found: Ba, 19·8; Equiv., 343·6. $(C_8H_7O_6S)_2$ Ba, $5H_2O$ requires Ba, 19·9 per cent. Equiv., 344·7.)

The *Methyl Ether.*—(*i*) Methyl ether of *m*-cresotic acid (20 g.) was dissolved in fuming sulphuric acid (25 g.) at room temperature and then heated at 60° for ½ hour. The sulphonic acid separated on absorbing moisture from air for three days. It was filtered through flannel and crystallised from water in needles or plates, m.p. 193° (decomp.). (Found: Equiv., 140·7. $C_9H_{10}O_6S, 2H_2O$ requires Equiv., 141·0).

(*ii*) It was also prepared by adding dimethylsulphate (200 c.c.) to a solution of sulpho-*m*-cresotic acid (25 g.) in sodium hydroxide solution (25%) at room temperature, until the reaction mixture gave no colour with ferric chloride, then heating on sand-bath for 2 hours, cooling and acidifying. (Found: Na, 7·6; H_2O, 11·3; Equiv., 305·6. $C_9H_9O_6SNa, 2H_2O$ requires Na, 7·6; H_2O, 11·8; per cent. Equiv., 304·0).

2:4:6-*Tribromo*-m-*cresol*, prepared by bubbling bromine vapour

(9 g.) through an aqueous solution of sulpho-*m*-cresotic acid (5 g.), crystallises as slender needles, m.p. 84°, (*cf.* Errera, *Ber.*, 1899, **32**, 2791 ; *J. pr. Chem.*, 1889, **39**, 59). (Found : Equiv., 339·2 ; Calc. for $C_7H_5OBr_3$: Equiv., 344·9).

2:6-*Dibromo*-m-*cresotic Acid* was obtained as a flocculent precipitate by bubbling bromine vapour (6 g.) through a solution of sulphonic acid in dilute hydrobromic acid (22%). It crystallised from dilute acetic acid in slender needles, m.p. 234-35°. It is identical with the compound prepared by Errera (*Ber.*, 1899, **32**, 2791) and by Einhorn and Ehret (*Annalen*, 1897, **295**, 180). (Found : Equiv., 308·8· Calc. for $C_8H_6O_3Br_2$: Equiv., 309·9.)

2-*Bromo*-6-*sulpho*-m-*cresotic Acid.*—Bromine (9 g.) was bubbled through a solution of sulphonic acid (15 g.) in hydrobromic acid (100 c.c , 45%). After having removed the solid, which was 2 : 6-dibromocresotic acid, the mother liquor was treated with concentrated hydrochloric acid and placed in a freezing mixture, when the sulpho-bromo-*m*-cresotic acid separated out. It crystallised from hot water in slender needles, m.p. 183°· The yields are improved if the bromination is carried out at 0°, instead of 30°, or stronger hydrobromic acid is used as solvent. (Found : Br, 22·4; Equiv., 182·5, $C_8H_7O_6BrS$, $3H_2O$ requires Br, 21·9 per cent. Equiv., 182·5).

The Acid Potassium Salt crystallised in slender needles from hot water. (Found : K, 10·2; Equiv., 367·2. $C_8H_6O_6$ Br SK, H_2O requires K, 10·6 per cent. Equiv., 367·1)

The Acid Calcium Salt crystallised from boiling water in granules. [Found : Ca, 5·8; Equiv., 329·9. $(C_8H_6O_6SBr)_2Ca$ requires Ca, 6·1 per cent. Equiv., 330·1].

2-*Bromo*-m-*cresotic Acid* was prepared by distilling a solution of 2-bromo-6-sulpho-*m*-cresotic acid (5 g.) in concentrated sulphuric acid (90 c.c.) with superheated steam at 150°, until a solid began to separate in the distillate. It is sparingly soluble in cold water, but soluble in alcohol, acetic acid and water. It crystallised from dilute acetic acid as leaflets, m.p. 211°, yield 3 g. (Found : Br, 34·7; Equiv., 230·9. $C_8H_7O_3Br$ requires Br, 34·6 per cent. Equiv., 231·0).

The Sodium Salt crystallised from water in shining plates. (Found : Na, 7·6. $C_8H_6O_3BrNa$, $2H_2O$ requires Na, 7·9 per cent).

The Potassium Salt crystallised from water in slender white needles or scales. (Found : K, 14·4· $C_8H_6O_3BrK$ requires K, 14·5 per cent).

The Methyl ether.—Bromine vapour (6 g.) was bubbled through a solution of methyl ether of 6-sulpho-*m*-cresotic acid (10 g.) in hydrobromic acid (40%, 50 c.c.). It crystallised from dilute acetic acid in needles, m.p. 137-38°. (Found : Equiv., 246·5. $C_9H_9O_3Br$ requires Equiv., 244·9).

The Barium Salt is sparingly soluble in water and difficult to crystallise. [Found : Ba, 20·4; H_2O, 5·2. $(C_9H_8O_3Br)_2$ Ba, $2H_2O$ requires Ba, 20·7 ; H_2O, 5·4 per cent].

2: 6-*Dinitro*-m-*cresotic Acid.*—A mixture of concentrated sulphuric acid (10 c.c.) and fuming nitric acid (10 c.c.) was added drop by drop with constant stirring to a solution of 6-sulpho-*m*-cresotic acid (20 g.) in concentrated sulphuric acid (30 c.c.) in a freezing mixture. After the reaction was complete the mixture was poured over powdered ice and the precipitate was recrystallised from dilute acetic acid in cubes, m.p. 185° (dinitro-*m*-cresotic acid); while the 2-nitro-6-sulpho-*m*-cresotic acid could be recovered from the mother liquor as the barium salt. A slight rise in the temperature gave dinitro-*m*-cresotic acid as the main product, while above 70°, it gave trinitro-*m*-cresol, m.p. 105°.

2-*Nitro*-6 *sulpho*-m-*cresotic Acid.*—A mixture of fuming nitric acid (5 g.) and fuming sulphuric acid (30 g.) was added drop by drop to *m*-cresotic acid (15 g.) dissolved in fuming sulphuric acid (50 g.) at room temperature when the nitrosulpho-*m*-cresotic acid crystallised out. It crystallises from hot water in slender needles, m p. 85°.

The *Barium Salt* was obtained by treating the mother liquor from the above experiment with barium carbonate. It crystallises in pale yellow needles from water. (Found : S, 6·5 ; Ba, 28·4. $C_8H_5O_8NSBa$, $4H_2O$ requires S, 6·6; Ba, 28·3 per cent).

The *Calcium Salt* crystallises in slender, pale yellow needles. (Found: Ca, 10·40. $C_8H_5O_8NS$ Ca, $4H_2O$ requires Ca, 10·3 per cent).

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Derivatives of 1-Hydroxy-2-naphthoic Acid. Part II. 4-Halogeno-1-methoxy-2-naphthoic Acids and their Derivatives.

BY G. V. JADHAV AND S. N. RAO.

In continuation of our work (Jadhav, Rao and Hirwe, *J. Indian Chem. Soc.*, 1936, **13**, 609) the methyl ethers of 4-halogeno-1-hydroxy-2-naphthoic acids are studied in this paper. The methylation of these acids by the usual method of dimethylsulphate in alkaline solution being unsuccessful, 1-methoxy-2-naphthoic acid was halogenated. This behaviour of the 4-halogeno-naphthoic acids compares well with the 3 : 5-disubstituted salicylic acids.

The methyl ether of 1-hydroxy-2-naphthoic acid was prepared according to Froelicher and Cohen (*J. Chem. Soc.*, 1922, **121**, 1654) by methylating methyl 1-hydroxy-2-naphthoate. The yield of the ester has been considerably improved by obtaining it through 1-hydroxy-2-naphthoyl chloride(Anschutz, Weber and Runkel, *Annalen*, 1906, **346**, 361). The methoxy acid was halogenated and the constitution of the halogeno acids confirmed by demethylating them to the corresponding 4-halogeno-1-hydroxy 2-naphthoic acid (Jadhav, Rao and Hirwe, *loc. cit.*). Various derivatives of these acids have been described.

EXPERIMENTAL.

Methyl 1-hydroxy-2-naphthoate.—To 1-hydroxy-1-naphthoyl chloride (from 20 g. of the hydroxy acid) methyl alcohol (40 c.c.) was slowly added and the ester obtained (15 g.) crystallised from rectified spirit as pale yellow needles, m.p. 77-78° (Schmitt and Burkard, *Ber.*, 1887, **20**, 2700 ; Cohen and Dudley, *J. Chem. Soc.*, 1910, **97**, 1747).

4-*Bromo*-1-*methoxy*-2-*naphthoic Acid.*—Bromine (10 g.) in acetic acid (40 c.c) was slowly added with stirring to 1-methoxy-2-naphthoic acid (10 g.), prepared by the method of Froelicher and Cohen (*loc.cit.*), in acetic acid (70 c.c.). The bromo acid (12-13 g.), which slowly separated out, crystallised from rectified spirit as white shining needles, m. p. 196-97°. (Found : Br, 28·2. $C_{12}H_9O_3Br$ requires Br, 28·5 per cent).

Demethylation of 4-Bromo-1-methoxy-2-naphthoic Acid.—Acetic anhydride (5 c.c.) was slowly added to a mixture of the bromomethoxy acid (0·5 g.) and hydroiodic acid (*d* 1·5, 5 c.c.), and the mixture heated at 100° for 1 hour. This mixture was treated with water and the solid obtained crystallised from acetic acid in white needles, m. p. 239-40° (decomp.), mixed m. p. with an authentic sample of 4-bromo-1-hydroxy-2-naphthoic acid.

4-Bromo-1-methoxy-2-naphthoyl Chloride.—A mixture of the bromomethoxy acid (3 g.), dry light petroleum ether (12 c.c.), dry benzene (3 c.c.) and phosphorus pentachloride (3 g.) was gently heated on the water-bath, until a clear solution was obtained. On cooling the naphthoyl chloride separated in white needles, which were filtered and washed with dry light petroleum ether and dried over phosphorus pentoxide, m. p. 114-15°. [Found : Total halogen calc. as Cl, 27.7; (by analysis of silver halides), Cl, 12·0, Br, 27·1. $C_{12}H_8O_2BrCl$ requires Cl, 11.9; Br, 26·7 per cent).

4-Chloro-1-methoxy-2-naphthoic Acid.—Dry chlorine gas (3.5 g.) was passed into a mixture of 1-methoxy-2-naphthoic acid (10 g.) in acetic acid (150 c.c.). The separated solid (7 g.) crystallised from rectified spirit in white shining needles, m. p. 182-83°. (Found : Cl,14·8. $C_{12}H_9O_3Cl$ requires Cl, 15·0 per cent).

The constitution of the chloromethoxy acid was proved in the same way as its bromo isomer by demethylating it to 4-chloro-1-hydroxy-2-naphthoic acid, m.p. 231-32° (decomp.).

4-Chloro-1-methoxy-2-naphthoyl Chloride was prepared in the same way as its bromo isomer; white needles, m.p. 106-7°. (Found: Cl, 27·8. $C_{12}H_8O_2Cl_2$ requires Cl, 27·9 per cent).

The phenyl and β-naphthyl esters of the 4-halogeno-1-methoxy-2-naphthoic acids were prepared by heating a mixture of the halogeno acid with the respective phenol and phosphorus oxychloride at 110-20° to a clear solution and the ester obtained on treating it with water.

The alkyl esters were obtained by heating either the silver salt of the acid or the naphthoyl chloride with the respective alkyl iodide or alcohol.

The arylamides were obtained by treating a benzene solution of the naphthoyl chloride with the respective amine.

TABLE I.

Derivatives of 4-Bromo-1-methoxy-2-naphthoic Acid.

Name.	Formula.	Crystallised from.	Appearance.	M.p.	Analysis. Found.	Analysis. Calc.
Phenyl ester	$C_{18}H_{13}O_3Br$	Alcohol	White shining needles	88-89°	Br, 22·5%	22·4%
β-Naphthyl ester	$C_{22}H_{15}O_5Br$	Acetic acid	Small white needles	114-15°	19·7	19·7
Ethyl ester	$C_{14}H_{13}O_3Br$	Alcohol	White needles	78-79°	26·2	25·9
Methyl ester	$C_{13}H_{11}O_3Br$	,,	Pinkish needles	96-97°	27·2	27·1
Anilide	$C_{18}H_{14}O_2NBr$	,,	White needles	123-24°	Br, 22·7 N (micro), 4·0	22·5 3.9
o-Toluidide	$C_{19}H_{16}O_2NBr$	Acetic acid	White plates	142-43°	Br, 21·6	21·6
m-Toluidide	,, ,,	Alcohol	White needles	122-23°	21·6	21·6
p-Toluidide	,, ,,	,,	,,	143-44°	21·9	21·6

TABLE II.

Derivatives of 4-Chloro-1-methoxy-2-napthoic Acid.

Name.	Formula.	Crystallised from.	Appearance.	M.p.	Analysis. Found.	Analysis. Calc.
Phenyl ester	$C_{18}H_{13}O_3Cl$	Alcohol	White needles	74-75°	Cl, 11·2%	11·4%
β-Naphthyl ester	$C_{22}H_{15}O_3Cl$	Acetic acid	,,	112-13°	10·0	9·8
Ethyl ester	$C_{14}H_{13}O_3Cl$	Alcohol	Small white needles	77-78°	13·2	13·4
Methyl ester	$C_{13}H_{11}O_3Cl$	,,	White needles	83-84°	14·1	14·2
Anilide	$C_{18}H_{14}O_2NCl$	,,	Shining white needles	105-6°	Cl, 11·4 N (micro), 4·6	11·4 4·5
o-Toluidide	$C_{19}H_{16}O_2NCl$	,,	Thick needles	134-35°	Cl, 11·1	10·9
m-Toluidide	,,	,,	White shining needles	116-17°	11·1	10·9
p-Toluidide	,,	,,	Small white needles	113-14°	11·0	10·9

The micro analyses were carried out by Dr. J. N. Ray of Lahore.

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Synthesis of Coumarins and Chromones from 4-Chloro- and 4-Bromo-1-naphthol.

By Duhkhaharan Chakravarti and Phanindra Nath Bagchi.

Clayton (*J. Chem. Soc.*, 1908, **93**, 2018) observed that in condensations of phenols with β-ketonic esters the presence of a halogen atom in the phenolic nucleus greatly hinders Pechmann's reaction forming coumarins and it was found by Chakravarti (*J. Indian Chem. Soc.*, 1932, **9**, 25,31) that the introduction of a negative substituent like Cl or NO_2 in monohydric phenols favours Simonis' reaction forming chromones. Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, **12**, 622) found, however, that negative substituents like Cl or NO_2 in the molecule of resorcin, which has the faculty of the formation of coumarins with great readiness, are not prejudicial to the formation of coumarins: chlororesorcin condenses with acetoacetic esters, irrespective of the complexity of the α-alkyl substituent, forming coumarins either in presence of sulphuric acid (Pechmann's reaction) or phosphorus pentoxide (Simonis' reaction).

In view of the fact that α-naphthol shows much reactivity in the formation of coumarins such that even by changing the condensing agent for phosphorus pentoxide it condenses with β-ketonic esters yielding coumarins and not chromones (Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 407) the condensations of the halogenated α-naphthols with acetoacetic esters have been studied in order to see whether there is any hindrance to the coumarin formation and the chromone formation is facilitated due to the presence of the halogen atom.

4-Chloro-1-naphthol, prepared by a modification of the method of Kast (*Ber.*, 1911, **44**, 1337. *vide* experimental) by the action of sulphuryl chloride on a hot chloroform solution of α-naphthol, condenses with acetoacetic ester and α-chloro-acetoacetic ester to form 6-chloro-4-methyl-1:2-αβ-naphthapyrone* (I, R = H; R′ = Me) and 3:6-dichloro-4-methyl-1:2-αβ-naphthapyrone respectively in a yield of 90% and identical coumarins are also obtained using phosphorus pentoxide as the condensing agent.

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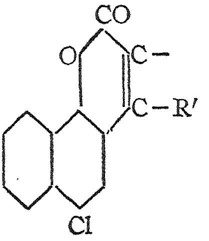
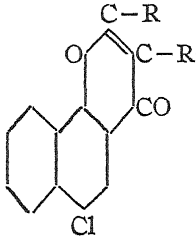
* The naphthapyrones, described in this paper, have been named according to the nomenclature proposed by Dey and Lakshminarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 153.

It is, however, remarkable that with the introduction of an alkyl substituent in the acetoacetic ester molecule as in the case of methyl-, ethyl-, propyl-, *iso*butylacetoacetic esters 4-chloro-1-naphthol gives in the presence of sulphuric acid a coumarin (I, R = Me, Et, Pr, C_4H_9; R′ = Me), but using phosphorus pentoxide the corresponding chromone (II, R = Me; R′ = Me, Et, Pr, C_4H_9) is obtained, not a trace of coumarin being formed. All these chromones contain a reactive methyl group in the 2-position, hence they are easily characterised by the formation of crystalline styryl derivatives (II, R = $CH{:}CH{\cdot}C_6H_5$; R′ = Me, Et, Pr, C_4H_9) when condensed with benzaldehyde in presence of alcoholic sodium ethoxide, while the corresponding isomeric 4-methylcoumarins are unchanged by this treatment (*cf.* Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2569 and Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129).



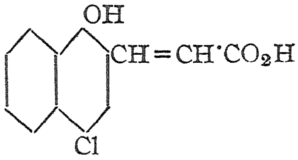
(I)



(II)

4-Chloro-1-naphthol has also been condensed with benzyl-acetoacetic ester, α-phenyl-acetoacetic ester, benzoyl acetic ester, acetosuccinic ester and acetone dicarboxylic acid to give coumarins. The condensations of 4-chloro-1-naphthol with acetoacetic ester and methyl-acetoacetic ester have been studied with different condensing agents, e.g. sodium acetate, sodium ethoxide, phosphoric acid, etc., and it has been found that, if condensation takes place at all, coumarins are always formed and not chromones (*cf.* Chakravarti, *J. Indian Chem. Soc.*, 1935, **12**, 536).

Incidentally, it may also be noted that 4-chloro-1-naphthol condenses with malic acid with as much ease as α-naphthol to yield 6-chloro-1 : 2-αβ-naphthapyrone (I, R=R′=H) which undergoes inversion to naphtha-*o*-coumaric acid (III) when heated with mercuric oxide in alkaline solution (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, **7**, 247).



(III)

4-Bromo-1-naphthol (Reverdin and Kaufmann, *Ber.*, 1895, **28**, 3049) behaves similarly to 4-chloro-1-naphthol with the only difference that the reactions are generally less smooth in the case of bromonaphthol and considerable amounts of tarry matter are invariably produced, which render the isolation of the product more difficult.

Thus, the study of the condensation of the halogenated α-naphthols with the acetoacetic esters brings the following facts into prominence :

(1) Three factors namely (*a*) the nature of the phenol, (*b*) the nature of the condensing agent, and (*c*) the nature of the β-ketonic ester determine the course of the condensation of a phenol with a β-ketonic ester to form a coumarin or a chromone.

(2) The results are in full agreement with the generalisation made by Chakravarti (*J. Indian Chem. Soc.*, 1932, **9**, 31) regarding the nature of the product to be obtained by Simonis' reaction.

(3) The 2-methyl group in the 1:4-αβ-naphthapyrones is always reactive and this is a distinctive test from the isomeric 4-methyl-1:2-αβ-naphthapyrones.

(4) The 1:4-αβ-naphthapyrones, described in literature (*cf.* Bhullar and Venkataraman, *J. Chem. Soc.*, 1931, 1165), have been prepared by Allan and Robinson's method (*J. Chem. Soc.*, 1924, **125**, 2192), but the condensation of 4-chloro-1-naphthol with β-ketonic esters has furnished a ready method for the synthesis of substituted 1:4-αβ-naphthapyrones.

EXPERIMENTAL.

Preparation of 4-Chloro-1-naphthol (*cf.* Kast, *loc. cit.*).—Sulphuryl chloride (55 g.), diluted with chloroform (25 c.c.), was added drop by drop from a dropping funnel to a hot solution of α-naphthol (60 g.) in chloroform (90 c.c.), when vigorous reaction set in with evolution of sulphur dioxide and hydrogen chloride. After all the sulphuryl chloride had been added the solution was boiled for a few minutes on a water-bath and left overnight. The colourless needles, separating, were filtered and crystallised from chloroform, m.p. 120-21°, yield 20-25 g.

6-*Chloro*-1:2-*αβ*-*naphthapyrone*.—A mixture of 4-chloro-1-naphthol (8 g.) and malic acid (7 g.) was heated carefully on wire-gauze with sulphuric acid (*d* 1·84, 20 c.c.) (*cf.* preparation of umbelliferone, Dey, Rao and Seshadri, *J. Indian Chem. Soc.*, 1934, **11**, 746). The mixture began to froth in a few minutes and heating was continued until the liquid became clear. After cooling the mixture was poured into ice, the solid collected, washed with 2*N*-caustic soda and crystallised from dilute acetic acid as colourless needles, m.p. 163°. (Found : Cl,* 15·50. $C_{13}H_7O_2Cl$ requires Cl, 15·40 per cent).

7-*Chloro*-*α*-*naphtha*-o-*coumaric Acid*.—A solution of 6-chloro-1:2-αβ-naphthapyrone (2 g.) in caustic potash solution (30 c.c., 16%) was diluted to 600 c.c. and boiled for 1 hour with powdered yellow mercuric oxide (2·5 g.). The solution was filtered and acidified with hydrochloric acid and the yellow precipitate dissolved in ammonia and the solution again acidified. The substance was crystallised from dilute alcohol as fine yellow needles, m.p. 185° (decomp.). The ammoniacal solution has a deep green fluorescence. (Found : Cl, 14·37. $C_{13}H_9O_3$ Cl requires Cl, 14·29 per cent).

6-*Chloro*-4-*methyl*-1:2-*αβ*-*naphthapyrone*.—To a mixture of 4-chloro-1-naphthol (4 g.) and acetoacetic ester (4 c.c.), cooled in ice, sulphuric acid (*d* 1·84, 8 c.c.) was slowly added with constant shaking. The solution was kept overnight and poured on to ice, when a greenish solid separated. This was collected, treated with 2 *N*-caustic soda, filtered and washed with water. It crystallised from glacial acetic acid (charcoal) as colourless needles, m.p. 219°, yield 5 g. (Found : Cl, 14·87. $C_{14}H_9O_2Cl$ requires Cl, 14·52 per cent).

The same compound was also obtained by using phosphorus pentoxide, sodium ethoxide and sodium acetate as condensing agents. No condensation was effected with phosphoric acid.

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* The chlorine in the compounds, described in this paper, has been estimated by the semi-micro method (ter Meulen, *Rec. trav. chim.*, 1928, **47**, 698).

6-Chloro-3:4-dimethyl-1:2-αβ-naphthapyrone, obtained from 4-chloro-1-naphthol (4 g.) and methyl-acetoacetic ester (4 g.) using sulphuric acid (*d* 1·84, 8 c. c.) in the usual manner, crystallised from glacial acetic acid as colourless needles, m. p. 203-4°, yield 2·8 g. (Found : Cl, 14·08. $C_{15}H_{11}O_2$ Cl requires Cl, 13·73 per cent). No condensation product could be isolated by condensing 4-chloro-1-naphthol with methyl-acetoacetic ester using sodium ethoxide as condensing agent ; with sodium acetate as condensing agent an insoluble amorphous product was isolated which could not be crystallised.

6-Chloro-2 : 3-dimethyl-1 : 4-αβ-naphthapyrone.—A mixture of 4-chloro-1-naphthol (5 g.), methyl-acetoacetic ester (5 c. c.) and phosphorus pentoxide (20 g.) was heated on the water-bath for 1 hour. The highly coloured mass was treated with water and the thick semi-solid product was washed with 2*N*-caustic soda solution, when a solid mixed with tarry matter was obtained. It crystallised from dilute acetic acid as pale yellow needles, m. p. 181-83°. (Found : Cl, 13·49. $C_{15}H_{11}O_2$ Cl requires Cl, 13·73 per cent). The solid, obtained by diluting the mother-liquor, was repeatedly crystallised from rectified spirit but no other product could be isolated.

6-Chloro-3-methyl-2-styryl-1 : 4-αβ-naphthapyrone.— A solution of the above 1:4-naphthapyrone in alcohol was heated on the water-bath with alcoholic solution of sodium ethoxide and benzaldehyde. The solution on being diluted by a few drops of water deposited a yellow substance, which crystallised from glacial acetic acid, m. p. 188-90°. (Found : Cl, 10·48. $C_{22}H_{15}O_2$ Cl requires Cl, 10·24 per cent).

The other 1:2- and 1:4- naphthapyrones, prepared from 4-chloro 1-naphthol, are described in Table I.

1:2- and 1:4-*Naphthapyrones from 4-Bromo-1-naphthol.*— 4-Bromo-1-naphthol was condensed with acetoacetic ester and α-alkylacetoacetic esters in presence of sulphuric acid or phosphorus pentoxide as condensing agents as in the case of 4-chloro-1-naphthol and the products obtained are described in Table II.

TABLE I.

Naphthapyrones from 4-Chloro-1-naphthol.

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Analysis. Found.	Req.	Remarks.
6-Chloro-4-methyl-3-ethyl-1 :2-αβ-naphthapyrone	$C_{16}H_{13}O_2Cl$	Ethyl-acetoacetic ester and 4-chloro-1-naphthol	H_2SO_4	129-30°	Cl, 13·30%	13·02%	Crystallised from dilute alcohol as light yellow needles.
6-Chloro-2-methyl-3-ethyl-1 :4-αβ-naphthapyrone (I)	$C_{16}H_{13}O_2Cl$	,,	P_2O_5	167-68°	13·26	13·02	Light yellow needles from rectified spirit.
6-Chloro-2-styryl-3-ethyl-1 :4-αβ-naphthapyrone	$C_{23}H_{17}O_2Cl$	(I) and benzaldehyde	NaOEt	194-95°	10·07	9·85	Crystallised from glacial acetic acid.
6-Chloro-4-methyl-3-propyl-1 :2-αβ-naphthapyrone	$C_{17}H_{15}O_2Cl$	Propyl-acetoacetic ester and 4-chloro 1-naphthol	H_2SO_4	104-5°	12·23	12·39	Crystallised from rectified spirit.
6-Chloro-2-methyl-3-propyl-1 :4-αβ-naphthapyrone (II)	$C_{17}H_{15}O_2Cl$	,,	P_2O_5	126-27°	12·60	12·39	Colourless shining needles from rectified spirit
6-Chloro-2-styryl-3-propyl-1 :4-αβ-naphthapyrone.	$C_{24}H_{19}O_2Cl$	(II) and benzaldehyde	NaOEt	228°	9·63	9·48	Light yellow needles from glacial acetic acid
6-Chloro-4-methyl 3-*iso*butyl-1 :2-αβ-naphthapyrone	$C_{18}H_{17}O_2Cl$	*iso*Butyl-acetoacetic ester and 4-chloro-1-naphthol	H_2SO_4	136-38°	12·04	11·81	Crystallised from rectified spirit

8

Table I (contd.).

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Analysis.		Remarks.
					Found.	Req.	
6-Chloro-2-methyl-3-*iso*-butyl-1 :4-$\alpha\beta$-naphthapyrone (III)	$C_{18}H_{17}O_2Cl$	*iso*Butyl-acetoacetic ester and 4-chloro-1-naphthol	P_2O_5	120-22°	Cl, 11·62%	11·81%	Crystallised from dilute alcohol.
6-Chloro-2-styryl-3-*iso*-butyl-1 :4-$\alpha\beta$-naphthapyrone	$C_{25}H_{21}O_2Cl$	(III) and benzaldehyde	NaOEt	235-36°	9·40	9·14	Pale yellow needles from glacial acetic acid.
6-Chloro-4-methyl-3-benzyl-1 :2-$\alpha\beta$-naphthapyrone	$C_{21}H_{15}O_2Cl$	Benzyl-acetoacetic ester and 4-chloro-1-naphthol	H_2SO_4	200°	11·09	10·61	Colourless needles from glacial acetic acid. No product could be isolated using P_2O_5.
3 :6-Dichloro-4-methyl-1 :2-$\alpha\beta$-naphthapyrone	$C_{14}H_8O_2Cl_2$	α-Chloro-acetoacetic ester and 4-chloro-1-naphthol	H_2SO_4 or P_2O_5	257°	25·51	25·45	Crystallised from pyridine.
6-Chloro-4-phenyl-1 :2-$\alpha\beta$-naphthapyrone	$C_{19}H_{11}O_2Cl$	Benzoyl acetic ester and 4-chloro-1-naphthol	H_2SO_4	164°	11·34	11·58	Crystallised from dilute alcohol.
6-Chloro-4-methyl-3-phenyl-1 :2-$\alpha\beta$-naphthapyrone	$C_{20}H_{13}O_2Cl$	Phenyl-acetoacetic ester and 4-chloro-1-naphthol	H_2SO_4	215-16°	11·35	11·08	Pale yellow needles from glacial acetic acid.
6-Chloro-4-methyl-1 :2-$\alpha\beta$-naphthapyrone-3-acetic ester	$C_{18}H_{15}O_4Cl$	Acetosuccinic ester and 4-chloro-1-naphthol	H_2SO_4	181-84°	10·70	10·75	Colourless needles from absolute alcohol.
6-Chloro-1 :2-$\alpha\beta$-naphthapyrone-4-acetic acid	$C_{15}H_9O_4Cl$	Acetone discarboxylic acid and 4-chloro-1-naphthol	H_2SO_4	212° (decomp.)	12·50	12·30	Crystallised from glacial acetic acid.

TABLE II

Naphthapyrones from 4-Bromo-1-naphthol.

Name.	Formula.	Prepared from.	Condensing agent.	M. p.	Analysis. Found.	Analysis. Req.	Remarks.
6-Bromo-4-methyl-1 :2-αβ-naphthapyrone.	$C_{14}H_9O_2Br$	Acetoacetic ester and 4-bromo-1-naphthol	H_2SO_4 or P_2O_5	208°	Br, 27·24%	27·68%	Light yellow needles from glacial acetic acid.
6-Bromo-3 :4-dimethyl-1 :2-αβ-naphthapyrone	$C_{15}H_{11}O_2Br$	Methyl-acetoacetic ester and 4-bromo-1-naphthol	H_2SO_4	187-89°	25·72	26·40	Crystallised from pyridine.
6-Bromo-2 :3-dimethyl-1 :4-αβ-naphthapyrone (I)	$C_{15}H_{11}O_2Br$	,,	P_2O_5	211-12°	26·29	26·40	Colourless needles from dilute acetic acid.
6-Bromo-2-styryl-3-methyl-1 :4-αβ-naphthapyrone	$C_{22}H_{15}O_2Br$	(I) and benzaldehyde	NaOEt	233°	20·53	20·46	Crystallised from glacial acetic acid.
6-Bromo-4-methyl-3-benzyl-1 :2-αβ-naphthapyrone.	$C_{21}H_{15}O_2Br$	Benzyl-acetoacetic ester and 4-bromo-1-naphthol	H_2SO_4	175-76°	20·59	21·11	Light yellow needles from pyridine. No product could be isolated using P_2O_5.

The authors' best thanks are due to Prof. P. C. Mitter for giving them facilities to carry on this investigation.

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Received September 21, 1936

A Note on Solid Sugars from Mohuwa Flower Syrup.

BY D. G. WALAWALKAR.

Mohuwa (*Bassia Latifolia*) flower is claimed to contain a large percentage of sugars, especially sucrose. Church (*Nature*, 1886, **33**, 343) reported only 3·2% of cane sugar from air-dried flowers; Elsworthy (*J. Soc. Chem. Ind.*, 1887, 21) reported that the cane sugar content varies from 4·6-17·1% according to the locality from which the flowers are gathered. But Fowler and co-workers (*J. Ind. Inst. Sci.*, 1920, **3**, 81) report as much as 28·8% of sucrose. In order to exploit the commercial possibility of obtaining sucrose, if available, in such large quantities and in general to prepare solid sugars like jaggery from the Mohuwa syrup, the following experiments were conducted.

EXPERIMENTAL.

The analytical figures for sucrose and non-reducing sugars agreed with those of Fowler (*loc. cit.*). Attempts were made to prepare solids like jaggery by atomisation of the syrup on a hot plate and making composite briquettes with cane sugar and the syrup.

10 Lbs. of the flowers were treated with water (6 litres) and repeatedly leached out when a solution of 29 Brix was obtained. It was concentrated in vacuum to different strengths ranging from 54 to 84 Brix. The syrup was darker in colour.

300 C.c. of 32 Brix syrup was shaken with 6 g. of '*Suchar*' and boiled for 1 hour under stirring and then filtered. No appreciable decolourisation was obtained. Similar treatment with '*Bone char*' effected an appreciable removal of colour and a lighter syrup was obtained. Sulphur dioxide and chlorine after liming (to p_H 8) failed to decolourise. All attempts to crystallise even with seeding of pure sucrose and laevulose failed to start crystallisation.

Next the syrup was atomised by means of a small hand sprayer on a dry steam-heated aluminium sheet, 1/16″ thick. The spray dried immediately and could be scraped off into a powder. However, it rapidly absorbed moisture from air and after a while became syrupy.

Attempts were made to make briquetttes of sugar by using the Mohuwa syrup as a binding material to obtain a product similar to jaggery. Experiments were conducted with various proportions of sugar and syrup. Solid was obtained with 84% Brix syrup and sugar if they were in the ratio of 1: 2. A few representative data are given below:

Sugar.	Syrup.	Remarks.
240 g.	120 g.	Soft to touch
350	100	Hard and well-set jaggery
500	100	Solid, very hard cake

All syrups, prepared, showed *laevo*-rotation thus showing a preponderance of reducing sugars.

In view of the above experiments it is suggested that it is impossible to crystallise sucrose from Mohuwa flower syrup. Further it has to be noted that all workers so far have not directly obtained and estimated sucrose from the syrup. Riche and Remount (*J. Pharm. Chem.*, 1880, 215) mention that air-dried flowers contain 60% sugars of which $\frac{1}{7}$th is crystallisable. Even this is only an estimate and they have not obtained the crystallised product. It is not improbable, therefore, that what is usually taken as sucrose by indirect estimation may be higher saccharides and not sucrose.

SUGAR TECHNOLOGY LABORATORY,
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WALTAIR.

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Phenanthrene from 9-Hydroxyphenanthrene (A Note).

By Nripendra Nath Chatterjee.

9-Hydroxyphenanthrene (5 g.) (*J. Indian Chem. Soc.*, 1935, **12**, 418, 591) was heated in a flask in a metal-bath with selenium (5 g.) at 300-310° for 10 hours. The temperature was then raised to 330° in course of 6 hours and it was further heated at that temperature for 8 hours. The product was dissolved in alcohol and a saturated solution of picric acid added when a picrate (0·3 g.) was precipitated. It was filtered, washed and twice recrystallised from alcohol, m.p. 145°.

Phenanthrene, regenerated from pure picrate, melts at 100°. The identities of phenanthrene and its picrate were confirmed by mixed m.p. with authentic specimens.

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Review

Physical Chemistry—BY PROF. F. H. MACDOUGALL. PUBLISHED BY THE MACMILLAN COMPANY, 1936. PP. 721, PRICE 17/- NETT.

Professor MacDougall has achieved real success in presenting to the students of Physical Chemistry a clear account of this rapidly growing subject within the compass of a small text book. He is of opinion that even in a small book, the students should be given the opportunity of becoming acquainted with the elements of thermodynamics and its more important applications. The reviewer cordially endorses this view. There is another welcome departure. The subject of atomic structure has been dealt with more fully than is generally done in such books.

In the chapter on chemical kinetics, we miss, however, references to much of the modern work on homogeneous gas reactions. This is a fascinating branch in which even beginners take considerable interest, and a more thorough treatment may have been included with advantage. We have pleasure in recommending the use of this book in our Colleges and Universities.

J. C. G.

Titanweiss—BY DR. ING. KURT HEISE, WITH 13 FIGURES AND 27 TABLES. PUBLISHED BY VERLAG VON THEODOR STEINKOPFF, DRESDEN AND LEIPZIG, 1936. PRICE R. M. -6 ; BOUND—R. M. -7.

The book under review forms a part of the series "Report of the Progress of Technology," edited by Prof. Dr. B. Rassow, Leipzig. The industry of titanium white has, within the last few years, gained an unusual importance, both for its use as a pigment as well as for various other industrial purposes.

As a white pigment it has got many advantages over other similar pigments like zinc oxide, lithophone and white lead. Titanium white excels all other white pigments in its covering power. Besides, unlike white lead and zinc white, it is entirely non-poisonous.

Since 1916 a large number of workers have been working on the use of titanium white as a pigment and also for various other industrial purposes. It is always used as a composition or mixed pigment with barium sulphate. Sometimes a little zinc oxide or zinc sulphide is also added.

The book is divided into three chapters followed by an appendix.

The first chapter deals with the various methods of preparation of titanium dioxide from different raw materials.

In the second chapter the application and properties of titanium dioxide as a pigment and also as a material for various technical purposes have been described.

These latter are.—

1. Production of white enamel varnish.
2. Addition to synthetic plastics.
3. Preparation of cosmetics.
4. As a linoleum pigment.
5. As a filling material in paper industry.
6. Use in rubber industry.
7. As an agent for reducing the extra gloss on artificial silk.
8. For the production of siloxyd glasses etc.

The various physico-technical methods for testing the quality of titanium white pigment have been described in the third chapter. The methods of qualitative and quantitative analysis of the pigment and its paste, and the conditions in which it is supplied are discussed in the same chapter.

The appendix contains a short account of the chemistry of titanium and its compounds.

The book will be found very useful both to the technologists and research workers, and not less to the students of chemistry in general.

References to all important works on the subject have been given and a complete list of literature added at the end of each chapter.

P. R.

Chapters in Organic Chemistry—By S. V. Divekar. Published by the Standard Publishing Company, Bombay, 1936. Pp. 478+xxxiv. Price Rs. 7/8/-.

The book deals with several chapters in organic chemistry covering the syllabus prescribed by the University of Bombay. As the subjects dealt with are of a varied nature, *e.g.*, aliphatic, aromatic, hydroaromatic, heterocyclic, it has not been possible for the authors to give a detailed and exhaustive information about the subjects within the small compass of the book.

The author has also given an outline of the methods for the detection and estimation of commoner elements and radicals in organic compounds but the inclusion of figures in the quantitative experiments would have made the experiments more intelligible.

The book is provided with an Index of authors and a complete Index of subjects, but the former Index would have been more helpful if the book contained references to original literature.

The book is well-written and contains useful and often up-to-date information about the subjects dealt with and would be a valuable guide to students preparing for degree examinations of the Indian Universities.

D. C.

X-ray Investigation of the Crystals of *o*-Nitrodiphenylamine.

By Mata Prasad and Jagdish Shanker.

The crystals of *o*-nitrodiphenylamine ($C_6H_5 \cdot NH \cdot C_6H_4NO_2$) have been studied crystallographically and have been found to develop c{001}, q{011}, o{111} and sometimes b (010) faces. They belong to the rhombic bipyramidal class and the axial ratio is

a : b : c = 0·4678 : 1 : 0·6709 (Groth, "Chemische Krystallographie," V, p. 49).

The substance was prepared in the laboratory by heating for twelve hours a mixture of *o*-nitraniline (3 g.), bromobenzene (12 c.c.), potassium carbonate (1 g.) and a trace of cuprous iodide which acts as a catalyst (*Ber.*, 1907, **40**, 4545). The excess of bromobenzene was removed by steam distillation and the unacted *o*-nitrodiphenylamine separated as an oil which solidified on cooling. It was purified by repeated crystallisations from alcohol.

The crystals grow in thin hexagonal or rhombic plates from a solution of the substance in alcohol. In the flat face, the angle θ in the hexagonal, and the angles θ and ψ in the rhombic forms of the crystals were measured and their values were found to agree very closely with those calculated from the ratio a : b given above.

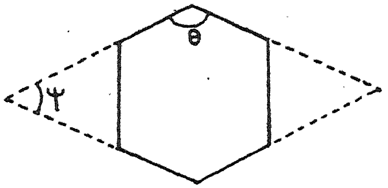


Fig. 1.

		Obs.	Cal.
θ	...	130°20′	129°52′
ψ	...	50°17′	50°8½′

This leaves no doubt that the flat face is the c(001) face in both the forms of the crystals. The measurement of other interfacial angles showed that the bounding faces are o{111} and q{011}.

TABLE I.

		Fock's obs. values (*cf.* Groth).	Authors' obs. values.	Values calc. taking b :c = 1 :0·6976.
o(111) : o′$(11\bar{1})$	=	62°34′	62°17′	62°33′
o(111) : o$(1\bar{1}1)$	=	42°30′	42°30′	42°27′
o(111) : q(011)	=	50°39′	..	50°43′
q(011) : c(001)	=	34°53′	35°8′	34°55′
o$(1\bar{1}1)$: q(011)	=	77°25′	...	77°22′

The crystals were examined by the rotation method using a Shearer gas tube and copper anticathode. The rotation photographs (Plates I, II and III) about the three axes gave the following values for the dimensions of the unit cell :

$$a = 6{\cdot}86\text{Å}, \qquad b = 14{\cdot}68\text{Å}, \qquad c = 10{\cdot}21\text{Å}$$

The axial ratio is

$$a : b : c = 0{\cdot}4673 : 1 : 0{\cdot}6956.$$

This ratio when compared with that given by Groth shows a large discrepancy in the value of $b : c$. But on recalculating this ratio from the interfacial angles observed by Fock (*cf.* Groth, *loc. cit.*, p. 49), it is found that

$$b : c = 1 : 0{\cdot}6976$$

which agrees very well with that found from the *X*-ray data.

In order to examine the halvings of planes, oscillation photographs were taken about the *a*, *b*, *c* axes and the spots were indexed by means of Bernal's chart (*Proc. Roy. Soc.*, 1926, **A 113**, 117). The following two tables give the planes observed and a relative idea of their intensity estimated by eye. The notations used have their usual significance.

FIG. 2.

Rotation photographs.

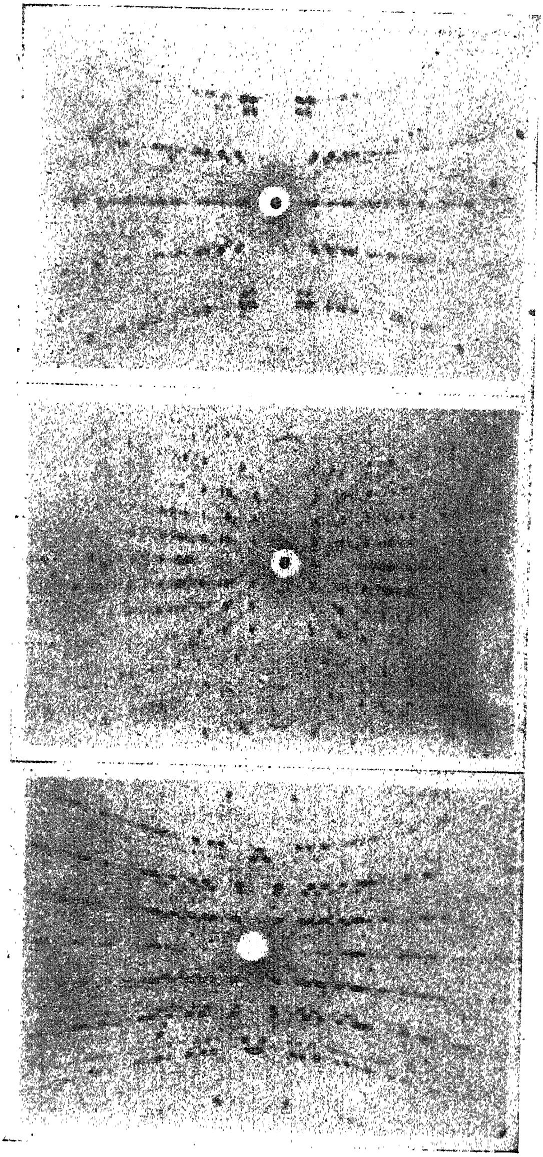


PLATE I
About *a*-axis
D=4·04 cm.

PLATE II
About *b*-axis
D=4·04 cm.

PLATE III
About *c*-axis
D=4·04 cm.

TABLE II.

Axial planes.	Prism planes. (okl).	Prism planes. (hol).	Prism planes. (hko).
001 v.s.	011 v.s.	201 s.	120 w.m.
002 m.	012 v.s.	202 m.s.	140 m.
003 w.	013 v.s.	203 m.	160 w.m.
004 w.	021 s.	204 w.m.	180 w.m., m.
005 m.	023 m.s.	401 w.m.	220 w.m.
020 w.	031 s.	402 w.m.	240 w.m.
040 v.w.	032 m.	403 w.	260 w.m.
060 v.w.	041 w.m.	......	280 w.m.
080 w.	042 w.m.	......	320 w.m.
200 s.	043 w.m.	......	340 w.m.
......	044 w.	......	360 v.w.
.....	045 v.w.	......	......
......	051 w.m.	......	......
......	052 w.m.	......	......
......	053 w.m.	......	......
......	055 w.	......	......
......	061 w.m.	......	......
......	062 w.m.	......	......
......	063 w.	......	......
......	064 m.s.	......	......
......	071 m.	......	......
......	073 v.w.	......	......
......	081 w.	......	......

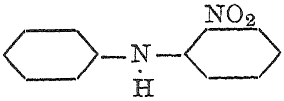
TABLE III.

General planes.

111 s.	211 s.	311 w.m.
112 s.	212 m.	312 w.m.
113 m.	213 v.w.	321 w.
114 m.	214 w.	322 w.
115 w.m.	215 v.w.	323 w.
121 v.s.	221 w.m.	333 v.w.
122 m.s.	222 m.	341 v.w.
123 m.	223 w.m.	342 w.m.
124 v.w.	224 w.m.	351 v.w.
125 v.w.	225 v.w.	352 v.w.
131 s.	231 w.m.	......
132 m.s.	232 w.	......
133 m.	234 v.w.	......
134 w.	241 v.w.	......
135 w.	242 w.m.	......
141 w.m.	243 w.m.	......
142 m.	244 w.	......
143 w.m.	251 w.	......
144 w.m.	252 w.	......
145 w.	253 m.	......
151 w.m.	254 v.w.	......
152 w.m.	261 w.	......
153 w.m.	262 w.	......
154 w.m.	263 v.w.	......
161 w.m.	264 v.w.	......
162 m.	271 v.w.	......
163 w.	......	......
164 v.w.	......	......
172 w.m.	......	......

Table I shows that (hol) planes are halved when h is odd, and (hko) are halved when k is odd. These halvings correspond to the space group Q_h^{11} with Γ_0 Bravais lattice (Astbury and Yardley, *Phil. Trans.*, 1924, **A224**, 221). The number of asymmetric molecules per unit cell required by the space group is eight, while the number of molecules of *o*-nitrodiphenylamine (Mol. wt., 214) calculated from the dimensions of the unit cell and the specific gravity of the crystals, which was found to be 1·366, is only four (accurately 3·97). The molecules, therefore, possess some element of symmetry and this may be a dyad axis of symmetry perpendicular to (001) or a plane of symmetry parallel to (100) or a centre of symmetry.

The molecule of *o*-nitrodiphenylamine is chemically represented as



and it is difficult to see from this representation the likelihood of the existence in the molecule of any of the three elements of symmetry required by the space group. It is possible, therefore, that the molecule of *o*-nitrodiphenylamine is an asymmetric one, in which case it cannot belong to the orthorhombic bipyramidal class, as in none of the space groups of this class, the number of asymmetric molecules required in the unit cell is four. Therefore only two possibilities remain to be considered (*i*) that the crystals may not belong to the orthorhombic system and (*ii*) that they may belong to some other group of the orthorhombic system.

(*i*) In order to decide the first possibility, the crystals were examined under a polarising microscope but no axial figures could be observed from the c (001) face. This observation is in agreement with the statement in Groth (*loc. cit.*). However, it is probable that the orthorhombic symmetry determined by goniometric measurements may not be confirmed by the internal arrangement of the molecules in the unit cell and these crystals may belong to the monoclinic system with an angle β differing from 90° by a few seconds. In that case the intensity of (hol) and (ho$\bar{l}$) planes should be different from each other. In the planes observed on the oscillation photographs about the three axes, the intensities of (hol) planes were observed to be the same as those of (ho$\bar{l}$) planes. However the differences in intensity, if any, may be small and have not been noticed by the eye and can only be discovered if intensity measurements of the spots are made.

(*ii*) As regards the second possibility the following are the only possible alternatives:

(*a*) The crystals may belong to the orthorhombic pyramidal class and to point group C_{2v}. On examining the abnormal halvings for those groups of this class which require four asymmetric molecules per unit cell (Astbury and Yardley's tables p. 233) it will be seen that the halvings observed do not correspond to any one of them. However for this class of crystals the symmetry axes *a* and *b* are interchangeable.

On doing this the observed abnormal halvings will be (*i*) (okl) halved when *k* is odd and (*ii*) (hko) halved when *h* is odd. These halvings also do not correspond to any of those mentioned in the tables.

(*b*) The crystals may belong to orthorhombic bispheroidal class and to the space group *Q*. In this class also there are no halvings corresponding to the ones observed in this investigation.

Thus the only possibility is that the crystals belong to the orthorhombic bipyramidal class and to the space group Q_h^{11}. In this class of crystals all the three axes *a*, *b* and *c* are interchangeable (Astbury and Yardley's tables p. 231) and the (hol) and (hko) planes in which halvings have been observed can change to the planes shown in the following table in which the corresponding nature of halvings is also indicated.—

TABLE IV.

	(1)	(2)	(3)	(4)
	(hol)	(okl)	(hko)	(hol)
Halved when	*h* is odd	*k* is odd	*h* is odd	*l* is odd
	(hko)	(hko)	(hol)	(okl)
Halved when	*k* is odd	*h* is odd	*l* is odd	*k* is odd

On referring to Astbury and Yardley's tables (pp. 234-235) it will be seen that no condition except (1) is possible. In that case the atoms constituting the molecule of *o*-nitrodiphenylamine are so arranged in the unit cell of the crystal that the molecule possesses one of the symmetry element characteristic of the group. Consequently the two rings were placed in space in various ways and each arrangement was examined for any possible molecular symmetry. The only arrangement possible is the one in which the two rings are placed in planes parallel to each other and there is geometrical plane of symmetry passing through the centres of the two nitrogen atoms. The two oxygen atoms of the nitro-group may be situated in any symmetrical position on either side of the symmetry plane. It is necessary to mention here that the carbon atom to which the nitro-group is attached and the one in the geometrically symmetrical position, are not identical with respect to the number of electrons associated with them.

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On the Relation between Peptisation of a Precipitate and its Electrokinetic Potential.

By Subodh Gobinda Chaudhury and Jyotirmoy Sen-Gupta

The phenomenon of peptisation is in a general way opposite to the process of coagulation and any theory that would attempt an explanation of the process of peptisation, should in more sense than one, be the reverse of the process of coagulation. An explanation on this basis was put forward by Freundlich ("Colloid and Capillary Chemistry," 1926, p. 472). Now recent researches on the cataphoretic velocity of colloidal particles in presence of electrolytes have generally shown (Mukherjee, Chaudhury and Bhabak, *J. Jndian Chem. Soc.*, 1936, **13**, 370; Mukherjee, Chaudhury and Sen-Gupta, *ibid.*, 1936, **13**, 421) that the rate of cataphoresis often increases as coagulation proceeds and that high cataphoretic speeds of colloids are usually observed at coagulating concentrations of electrolytes. These are facts that go against coagulation taking place at a low critical constant potential and as such the prevalent views regarding the phenomenon of coagulation require to be changed and it suggests that current views regarding peptisation may also require to be modified.

Buzagh (*Kolloid Z.*, 1929, **48**, 33; 1927, **41**, 169) working with suspensions of charcoal and ferric hydroxide found that for a definite concentration of a peptising electrolyte, the cataphoretic velocity increases to a maximum with increasing mass of the peptised substance and afterwards diminishes. Investigations were also carried out by Kruyt and van der Willigen (*Z. physikal. Chem.*, 1928, **139**, 53) who tried to extend the earlier considerations of Fajans (*Z. physikal. Chem.*, 1921, **97**, 478) and Mukherjee and his co-workers (*J. Indian Chem. Soc*, 1926, **3**, 335; 1927, **4**, 459). They observed that the electrokinetic potential of different substances can be increased by all kinds of electrolytes, but only those ions, which fit into the lattice of the particles, can peptise the substance (*cf.* also the work of Cysouw, mentioned by Verwey, *Chem. Rev.*, 1935, **16**, 363.) Before any explanation of these results can be advanced from the electrokinetic or the ion adsorption point of view it appears that the experiments on the general nature of the variations of the cataphoretic velocity of a precipitate during the course of its peptisation would throw considerable light on causes at work in such phenomena and on the mechanism of peptisation.

EXPERIMENTAL.

The systems studied are ferrocyanides and sulphides of a number of metals. In the case of the ferrocyanides of zinc, copper and uranium, no special peptising agents were used. The ferrocyanides were precipitated as follows :

I. The ferrocyanide solution A (0·1 *N*) is added to the other salt solution B (0·1 *N*)

(*i*) in equal volumes of 100 c.c. each ;
(*ii*) with 1 c.c. excess of A ; 101 c.c. of A and 100 c.c. of B ;
(*iii*) with 1 c.c. excess of B ; 100 c.c. of A and 101 c.c. of B.

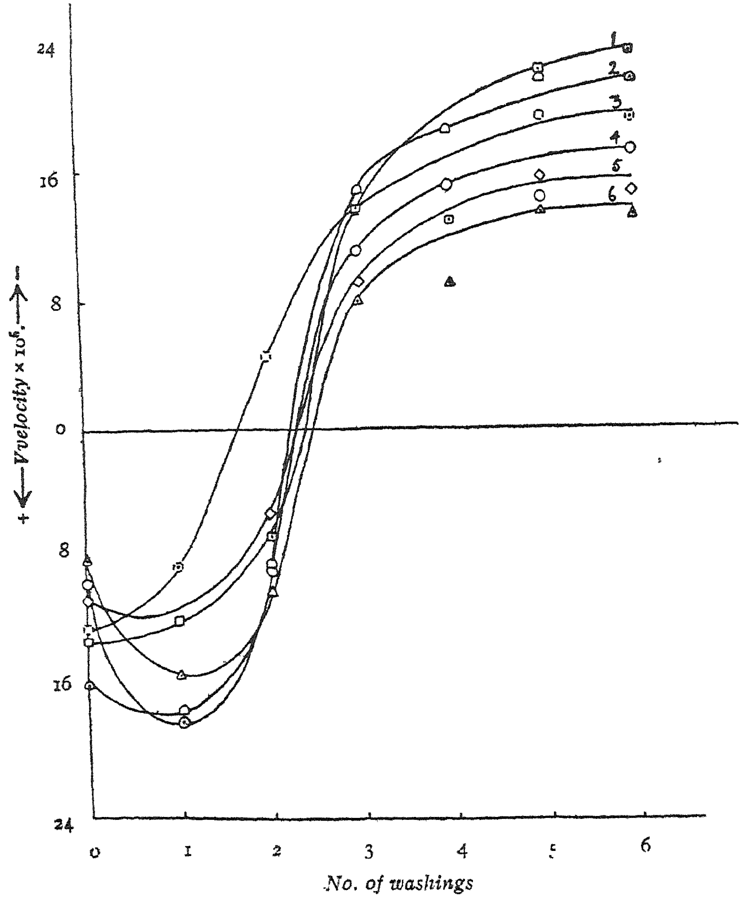
II. Solution B (0·1*N*) is added to the ferrocyanide solution A (0·1*N*).

(*i*) in equal volumes of 100 c.c. each ;
(*ii*) with 1 c.c. excess of A ; 100 c.c. of B and 101 c.c. of A ;
(*iii*) with 1 c.c. excess of B ; 101 c.c. of B and 100 c.c. of A.

The salts used for the precipitation of the respective ferrocyanides are (1) $CuSO_4, 5H_2O$; (2) $UO_2(NO_3)_2, 6H_2O$, (3) $ZnSO_4, 7H_2O$ and $K_4Fe(CN)_6, 3H_2O$. Thus the precipitate of each ferrocyanide was obtained in six different ways. The mixtures were centrifuged and the precipitates thrown down. The supernatant liquids were decanted off, 200 c.c. of fresh conductivity water were added to the precipitate and the contents thoroughly mixed by stirring. The cataphoretic velocities of the precipitates initially formed as well as of the particles suspended in fresh conductivity water after each washing were measured with the microcataphoretic apparatus described before (*cf*. Mukherjee, Chaudhury, and Bhabak, *loc. cit.*; Mukherjee, Chaudhury and Sen-Gupta, *loc. cit.*). The results are given in Figs. 1, 3, and 4. 0·01 *N*-potassium ferrocyanide and 0·01*N*-copper sulphate were also used. Since the amount of the precipitate was small, the wash liquid used each time was 100 c.c. The results are given in Fig. 2.

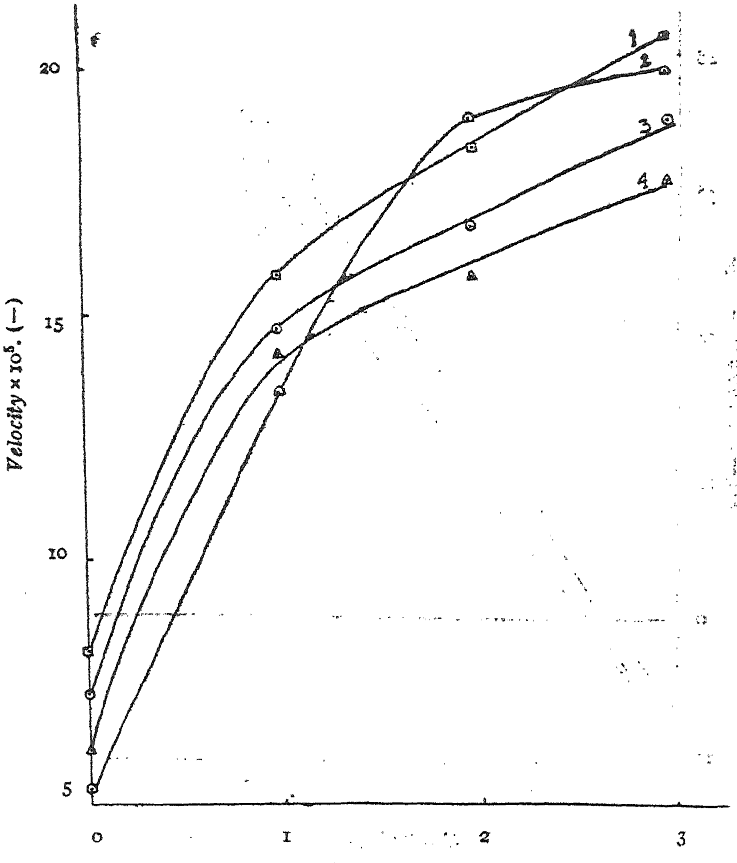
The sulphides were precipitated by passing hydrogen sulphide through solutions of their respective salts acidified with hydrochloric acid. The precipitates were washed by decantation with conductivity

FIG. I.



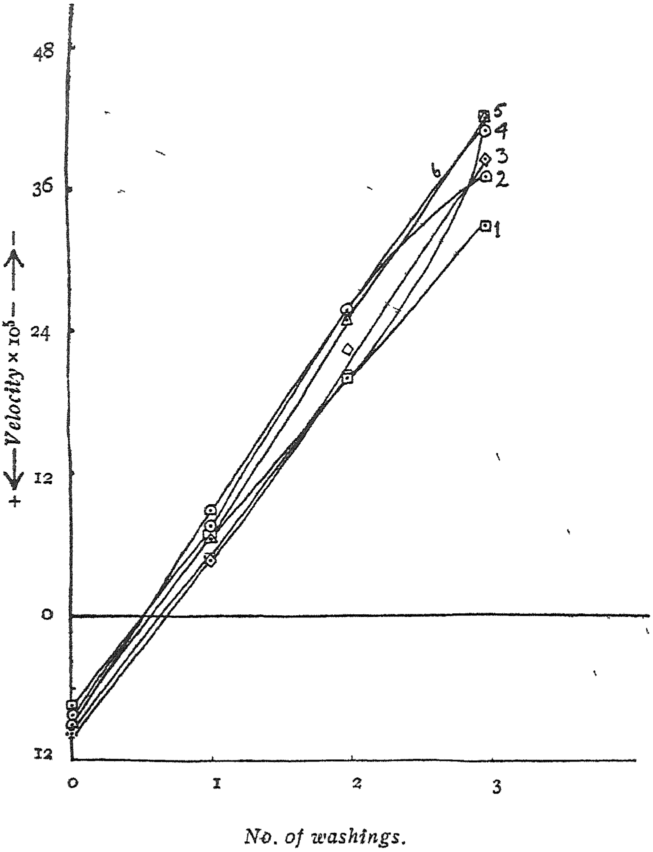
Curve 1—$K_4Fe(CN)_6$ added to $CuSO_4$ in equal vol.
2—$CuSO_4$ added to $K_4Fe(CN)_6$, latter in excess.
3—$K_4Fe(CN)_6$ added to $CuSO_4$, former in excess.
4—$CuSO_4$ added to $K_4Fe(CN)_6$ in equal vol.
5—$K_4Fe(CN)_6$ added to $CuSO_4$, latter in excess.
6—$CuSO_4$ added to $K_4Fe(CN)_6$, former in excess

FIG. 2.



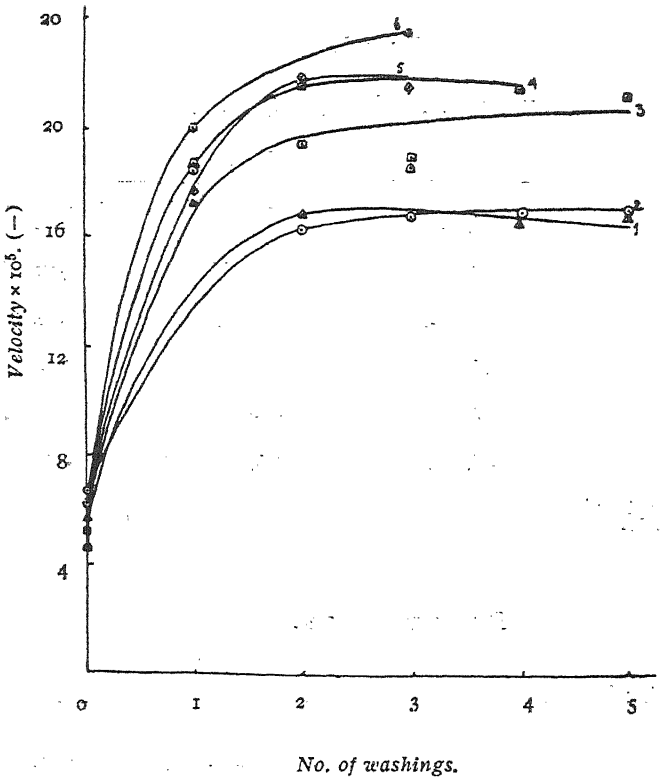
Curves 1—4 refer to $CuSO_4$ added to $K_4Fe(CN)_6$ in equal vol., $CuSO_4$ in excess, equal vol, and $K_4Fe(CN)_6$ in excess respectively.

FIG. 3.



Curve 1—$K_4Fe(CN)_6$ added to $UO_2(NO_3)_2$, former in excess
2—$UO_2(NO_3)_2$,, $K_4Fe(CN)_6$, latter in excess
3—$K_4Fe(CN)_6$,, $UO_2(NO_3)_2$ in equal vol.
4—$UO_2(NO_3)_2$,, $K_4Fe(CN)_6$ in ,, ,,
5—$K_4Fe(CN)_6$,, $UO_2(NO_3)_2$, latter in excess
6—$UO_2(NO_3)_2$,, $K_4Fe(CN)_6$, former in excess.

FIG. 4.



Curves 1—3 refer respectively to $ZnSO_4$ added to $K_4Fe(CN)_6$ with $K_4Fe(CN)_6$ in excess; in equal vols.; $ZnSO_4$ in excess. Curves 4—6 refer respectively to $K_4Fe(CN)_6$ added to $ZnSO_4$ (4)—in equal vols.; $ZnSO_4$ in excess; $K_4Fe(CN)_6$ in excess.

water and the c.v. again measured. Then hydrogen sulphide was passed through the solution and the c.v. measured again. Table I contains the results obtained.

TABLE I.

C. V. *of the sulphide precipitates.*

Substance	* V × 10^5		
	Just after precipitation.	After washing.	After passing H_2S.
1. As_2S_3	32·5 (N)	22·9 (N)	31·1 (P)
2. SnS_2	43·7 ,,	35·2 ,,	42·5 ,,
3. Sb_2S_3	23·2 ,,	20·9 ,,	38·2 ,,
4. HgS	29·6 ,,	27·6 ,,	39·3 ,,
5. CdS	14·7 ,,	12·4 ,,	28·0 ,,

(N) No peptisation.
(P) Peptisation.

DISCUSSION.

Relation between Electrokinetic Potential and Peptisation.

Results of different ferrocyanides (*cf.* Figs. 1 to 4) show that the cataphoretic velocity generally increases with the peptisation of a precipitate under all the above conditions of precipitation. The initial c.v. of the precipitate obtained, the nature of the variation of the c.v. of the precipitate before it peptises into a colloidal solution and the final c.v. of the colloid formed from the precipitate, however, depend on the conditions of precipitation.

The following observations require to be elucidated :—

(*i*) When 0·1*N*-$CuSO_4$ and 0·1 *N*-$K_4Fe(CN)_6$ are the precipitants, the initial charge is always positive but with the centinormal solutions as precipitants, the initial charge is always negative.

(*ii*) The initial charge of the uranium ferrocyanide precipitate is always positive. Decinormal solutions were used for precipitation.

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* The charge is always negative and is expressed in cm. per sec. per volt/cm.

(*iii*) The initial charge of zinc ferrocyanide is always negative.

(*iv*) The course of variation of the c.v. on repeated washings till peptisation takes place (*i.e.*, till the precipitate passes into a finer state of subdivision).

It has been suggested in earlier papers (*loc. cit.*) that the observed high cataphoretic speed at the coagulating concentrations of electrolytes is the result of aggregation. The phenomenon of coagulation consists of two processes, (*i*) agglomeration of the primary colloidal particles and (*ii*) the settling of the particles. The commencement of the first process may be easily explained by assuming that just after the addition of an electrolyte, the density of the charge on the colloid diminishes and this diminution helps aggregation of the colloidal particles. With aggregation, the cataphoretic velocity becomes higher and higher. Further agglomeration at this high density of charge requires to be explained. It might be assumed (*cf.* Freundlich, "Colloid and Capillary Chemistry," 1926, p. 434) that the larger particles act as nuclei, where particles of smaller size condense for the larger particles have got larger spheres of action. Or in the alternative it might also be assumed that with the irregular growth of the clusters of particles, charges on the so-called growing aggregates are accumulated at particular spots on the surface and further growth of the particles takes place with attachment of smaller particles at those places on the surface where the density of charge is either nil or very low.

After the particles have grown to a certain size, they are not affected any more by the brownian movement of the particles and due to the action of gravity they settle down and this explains the second part of the progress of coagulation. The final equilibrium is attained when no further aggregation occurs with time, and the latter particles already settled down acquire a low charge due to the adsorption of the oppositely charged ions (*cf.* Mukherjee, Chaudhury and Bhabak, *loc. cit.*). If the views on coagulation as set forth above be true, then the process of peptisation by washing with the solvent alone can be looked at in the case of ferrocyanide precipitates in the following way:—

By washing with the solvent, the electrolytes are removed and the density of charge tends to be high. (This, however, is not always the case as will be evident from the *initial* parts of some curves in Figs. 1 to 4 depending, of course, on the nature of the precipitate studied.)

As a result of this high density of charge of the individual small particles within the agglomerate, the agglomerate breaks up and we get particles of smaller size with high density of charge (cf., the steepness of the curves in all the figures, when it passes from the precipitate to the sol condition).

At this stage, small particles are subjected to the action of brownian movements and they are, therefore, suspended in the medium and further agglomeration is prevented due to the existence of this high density of charge of the particles formed.

In the case of sulphides (*cf.* Table I), the increment of charge with peptisation after passing hydrogen sulphide is easy to follow from the point of view developed above. *The initial decrease of the charge of the* precipitate after washing is, however, explicable by assuming that HS-ions primarily adsorbed on the surface are removed by washing.

SUMMARY.

1. The electrokinetic potential of the particles of a precipitate increases during peptisation.

2. A polar precipitate does not always show the same sign of charge as that of the constituent ion present in excess at the time of precipitation. The charge appears also to depend on the concentrations of the precipitants taken.

Our best thanks are due to Prof. J. N. Mukherjee, D.Sc., for his suggestions, guidance, and criticisms of this paper.

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Adsorptive Properties of Synthetic Resins.

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Synthetic resins, as a rule, are not composed of single entities but consist of macromolecules of varying size and are usually classed as "xerogels". The term has been applied to such natural colloids as cotton, wool, silk, hair, horn and such artifacts as gelatin, leather, charcoal, cellulose derivatives and to completely synthetic products such as phenol-formaldehyde resins and silica gel (Sheppard, *Trans. Faraday Soc.*, 1933, **29**, 77).

Barthelemy (*Chim. et Ind.*, 1926, **16**, 367) studied the behaviour of alcoholic suspensions of phenol-aldehyde resins under the influence of an electric field and observed that the alkaline-catalysed resins migrated to the cathode, while the acid catalysed ones to the anode. He regarded them therefore as ionic micelle. The growth of colloidal aggregates presumably occurs through the ionic nature of these particles. The sizes of the colloidal resin particles (Dubrisay, *Chim. et Ind.*, 1928, 666) range from the smallest, which can be detected by means of the ultramicroscope to the largest which are present in partial suspensions.

From the above evidence it is clear that synthetic resins possess colloidally disperse structures with a strongly developed inner surface. It would have been natural, therefore, to look for pronounced adsorptive properties in them. It is surprising, however, that no one, until recently, investigated this field of research. Credit is due to Adams and Holmes (*J. Soc. Chem. Ind.*, 1935, **54**, 1T) from Prof. Morgan's laboratories, who have studied the adsorption of a large number of cations from aqueous solutions of metallic salts by synthetic resins derived from polyhydric phenols and formaldehyde. They have observed considerable removal of antimony, bismuth, lead, mercury, silver, tin, vanadium, uranyl and methylene blue with one or other of the resins and came to the conclusion that these resins were generally superior to the recognised adsorbents like base exchange material and active carbon. The work of Adams and Holmes (*loc. cit.*) is that of pioneers in the field indicating new lines of investigation; their results, as they have themselves pointed out, are more or less qualitative and comparative in nature. It is obvious that this subject presents a most interesting scope for colloid-chemical investigations not only of theoretical, but also of practical interest and it has, therefore, been considered desirable to undertake a detailed quantitative study of adsorption on these new adsorbents from the following standpoints:—

1. Method of activation.
2. Effect of natures of solvent on adsorption.
3. Adsorption of non-or weakly dissociated substances in aqueous solution.
4. Adsorption of strongly dissociated substances in aqueous solutions, *e.g.*, mineral acids and bases.

EXPERIMENTAL.

Preparation of Resins—Phenol (2 parts), formalin (40%, 4 parts) and water (25 parts) were refluxed over a sand-bath and concentrated hydrochloric acid (1 part) was added. A violent reaction took place and the resin separated within a couple of minutes. It was filtered off and washed first with dilute mineral acid, and finally with hot water until the filtrate was free from all traces of acid, phenol and formaldehyde. The resin was dried in an air-oven at 100-110°, powdered and passed through a 90 mesh sieve. The powdered resin was placed in a vacuum desiccator over soda lime and repeatedly evacuated, after which treatment the resin was ready for use. The resins on incineration gave no ash.

The experimental technique of adsorption measurement consisted in setting up a series of equal volumes of solution of differing and measured concentration, C_0. Then, equal masses of the sorbent were placed in each solution. The systems were agitated for half an hour and allowed to remain until equilibrium was attained. After the sorbent had settled down, portions of the supernatant solution were analysed to determine the equilibrium concentration C_e. The amount of solute sorbed in each case was then taken to be $C_0 - C_e$. The amounts of adsorption, represented by x/m (expressed in milligram-equivalents per gram of adsorbent) in the tables are obviously not strictly accurate in as much as no attempt was made to correct for the adsorption of solvent. An error was undoubtedly introduced, but it must be very small as the solutions were very dilute and the adsorption of solvent would not materially alter the concentration.

Methods of Activation.—The effect of well known methods of activating adsorbents was studied on a recorsinol-formaldehyde resin and the results are given in Table I.

TABLE I.

Sorption from 50 c.c. 0·0753N-NaOH soln. by 0·5 g. of resin.

	Concentration.		Amount adsorbed x.	% sorption.	Increase in % sorption.
	Before sorption C_o.	After sorption C_e.			
Original resin	0·1507 g.	0·09305 g	0·05765 g.	38·24	...
Resin steamed	0·1507	0·0856	0·0651	43·19	4·95
Resin treated with 5% HCl and washed till filtrate showed absence of Cl′	0·1507	0·0846	0·0661	43·86	5·62
Resin heated at 140° under vacuum	0·1507	0·0921	0·0586	38·88	0·64
Resin evacuated for 2 hours	0·1507	0·0893	0·0614	40·74	2·50
Resin treated with NaOH and washed till the filtrate was neutral to litmus	0·1507	0·0912	0·0595	39·48	1·24

It is clear from the above table that the treatment with steam and 5% HCl increased the adsorptive capacity of the resin by about 5%. Though quantitative experiments were only tried for a solution of sodium hydroxide, it was noticed that the increase in adsorption was more or less general for all adsorbed materials.

Effect of the Nature of Solvent on Adsorption.—The sorption of a given solute by charcoal from a wide variety of solvents has been studied by various workers notably Freundlich (*Z. physikal. Chem.*, 1910, **73**, 385), Lundelius (*Kolloid Z.*, 1920, **26**, 145), Gurtvitsch (*Kolloid Z.*, 1623, **32**, 80; 1926, **38**, 247), Heymann and Boye (*Z. physikal. Chem.*, 1930, **150**, 219) in an attempt to explain the different degrees of adsorption from different solvents. Explanations have been offered based on surface tension, solubility, heats of wetting and molecular polarisation. While no general rule could be given, it was concluded from the results obtained that a solute is apt to be weakly sorbed from solvents in which it is very soluble, from solvents which wet the sorbent with high energy, and from solvents possessing weak dipole moments.

We have studied the sorption of benzoic acid from a number of solvents by a resorcinol-formaldehyde resin and the results are given in Table II.

TABLE II.

Sorption from 50 c. c. of 0·01639*N* benzoic acid soln. by 0·5 g. of resin in different solvents.

Solvent.	%Sorption.	Mol. polarisation. in cm³.	Dipole moment $M \times 10^{18}$ e.s.u.	Solubility of benzoic acid per 100 g. of the solvent at 25°.
CS_2	20·54	21·3	0	4·571
Benzene	1·683	26·3	0 (0·2)	11·605
CCl_4	13·87	28·1	0	3·965
MeOH	1·196	36·8	1·7 (1·15)	73·50
EtOH	1·819.	52·1	1·7 (1·53)	57·70
Acetone	2·213	63·7	2·6 (1·28)	55·60
Water	51·26	79·1	1·85	0·345

The values for dipole moments and molecular polarisations have been taken from the table of dipole moments collected by Sidgwick (*Trans. Faraday Soc.*, 1934, **30**, 905). It is obvious from Table II that though no definite rule, inter-relating the amount absorbed of a solute in various solvents to its solubility in them or to the dipole moment of the solvent, can be given, fair guesses can be made. In developing a general theory, account must be taken not only of the influence of the solvent on adsorbate but also its influence on the absorbent. The high adsorption from water is explained according to Freundlich ("Colloid and Capillary Chemistry," p 192) who stated "Water is characterised by a high surface tension and by a high interfacial tension against other liquids. We may therefore ascribe to it also a high interfacial tension against solids, especially hydrophobic solids. On the other hand, adsorption is low from organic liquids such as benzene, alcohol, etc., in the case of which we may assume, for similar reasons, a low interfacial tension against solids." If the solubility of a given adsorbate is the same in a number of different solvents, greater adsorption will occur from solutions, the solvent of which has higher interfacial tension against the adsorbent.

The difference in degree of sorption from different solvents may be used advantageously in the recovery of various substances from solutions. A dilute aqueous solution of a dye, like acridine orange can be readily and completely decolourised by the sorbent resin. If the resin is then placed in alcohol, from which acridine orange is sorbed less than from water, a large amount of it goes into solution in the alcohol. Further, it was observed that these resins showed a marked adsorptive capacity for alkaloid bases and this has been made use of in the extraction and purification of alkaloids. An aqueous solution of an alkaloid salt was treated with a sorbent resin and made slightly alkaline to liberate the alkaloid base which was strongly sorbed. The sorbent was removed and treated with an organic solvent which extracted a large part of the alkaloid. Quantitative experiments in this direction are being carried on and the results will be communicated in a later paper.

Adsorption of Non- or Weakly dissociated Substances in Aqueous Solution.

The adsorption of aromatic and aliphatic acids from aqueous solutions has been studied and the results are given in Tables III*a*, III*b* and IV. Table III*a* gives the percentage sorptions of various organic acids from aqueous solutions by a resorcinol-acetaldehyde resin and shows the following general effects :—

(*i*) Sorption of aromatic acids is greater than the sorption of aliphatic acids.

(*ii*) The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series.

(*iii*) Substituents such as -OH and-NH_2 lower the sorptive affinity.

TABLE III*a*.

Sorption of various organic acids from 50 c. c. of 0·12*N* aqueous solution by 1 g. of resin.

Adsorbed substance.	% Sorption.	Adsorbed substance.	% Sorption.
Benzoic acid	55·80%	Formic acid	1·431
Salicylic acid	50·03	Acetic acid	3·527
Anthranilic acid	40·09	Propionic acid	10·012
Picric acid	13·87	Butyric acid	14·32
		Amino-acetic acid	0·50
		Lactic acid	7·14

TABLE III *b*.

Sorption of aromatic acids from 50 c.c. solution by 1 g. of resorcinol-acetaldehyde resin.

Benzoic acid		Salicylic acid		Picric acid	
C_e.	x/m.	C_e.	x/m.	C_e.	x/m.
0·01029	0·4155	0·010580	0·3415	0·013860	0·1182
0·00901	0·3955	0·008925	0·3420	0·010470	0·1050
0·00701	0·3675	0·007010	0·3101	0·008337	0·09572
0·00539	0·3400	0·005819	0·2913	0·006586	0·08570
0·00470	0·3106	0·005174	0·2653	0·005508	0·07952
0·00390	0·2930	0·004529	0·2391	0·004462	0·07228
0·00323	0·2647	0·003815	0·2099	0·002869	0·05917
0·00259	0·2357	0·003239	0·1874	0·001591	0·04174
0·00204	0·2096	0·002643	0·1618		

TABLE IV.

Sorption of fatty acids from 60 c.c. of aqueous solution by 1 g. of resorcinol-acetaldehyde resin.

Formic acid		Acetic acid		Propionic acid		Butyric acid	
C_e.	x/m.	C_e.	x/m.	C_e.	x/m.	C_e.	x/m.
0·06800	0·06100	0·09700	0·2320	0·0958	0·3790	0·0798	0·4260
0·05600	0·05100	0·08401	0·2065	0·0830	0·3610	0·0540	0·3575
0·04948	0·04304	0·07208	0·1810	0·06808	0·3414	0·03932	0·3116
0·04124	0·03522	0·06010	0·1500	0·05656	0·2927	0·03274	0·2617
0·03298	0·02869	0·04801	0·1240	0·04500	0·2498	0·02616	0·2113
0·02477	0·01956	0·03626	0·0770	0·03369	0·1914	0·01932	0·1767
0·01647	0·01434	0·02425	0·0460	0·02215	0·1460	0·01272	0·1275
0·008237	0·006521	0·01250	0·0090	0·01130	0·0592	0·006125	0·07773

Tables III *b* and IV show the variation of absorption with concentration of aromatic and aliphatic acids respectively. The results for the three aromatic acids show that at the highest concentrations the adsorptions are approaching the saturation values. Those for the aliphatic acid show that the saturation values are attained much more slowly in these cases.

Adsorption of Strongly Dissociated Substances in Aqueous Solution.

(*a*) *Adsorption of Inorganic Bases.*—The adsorption from aqueous solutions of the sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate of concentrations varying from 0.1*N* to 0.01*N* has been studied. All experiments were repeated a number of times. The data given in Table V are averages of at least four independent determinations. It will be noted that typical adsorption isotherms are obtained. This indicates that adsorption or surface reactions must predominate. It seems probable that in these systems "chemical reactions" may and probably do occur, but they are limited to the surface only ; these reactions are, therefore, adsorptions of the "heteropolar" type which has been discussed by Freundlich ("Colloid and Capillary Chemistry," p. 287). With fairly dilute solutions used, there appears to be no reason to consider the process to be other than one of adsorption.

TABLE V.

Sorption of bases from 0.1*N*- aqueous solutions by 0·5 g. of resorcinol-formaldehyde resin.

Sodium hydroxide			Potassium hydroxide		
C_e.	*x*.	*x*/*m*.	C_e.	*x*.	*x*/*m*.
0·07630	2·370	4·740	0·07628	2·417	4·834
0·06655	2·345	4·690	0·06697	2·343	4·686
0·05722	2·277	4·554	0·05766	2·272	4·544
0·04744	2·225	4·450	0·04838	2·195	4·390
0·03862	2·137	4·274	0·03907	2·121	4·242
0·02970	2·030	4·060	0·03024	2·000	4·000
0·02185	1·814	3·628	0·02188	1·830	3·660
0·01348	1·652	3·304	0·01302	1·711	3·422
0·006024	1·397	2·794	0·006053	1·402	2·804
0·001375	0·8624	1·7248	0·001393	0·862	1·7248

TABLE V (contd.).

Sorption of bases from 0·1 *N*- aqueous solutions by 0·5 g. of resorcinol-formaldehyde resin.

Sodium carbonate			Potassium carbonate		
C_e.	*x*.	*x*/*m*.	C_e.	*x*.	*x*/*m*.
0·08880	1·0320	2·0640	0·08742	1·2120	2·4240
0·07956	0·9661	1·9322	0·07818	1·1380	2·2760
0·07021	0·9084	1·8168	0·06880	1·0810	2·1620
0·06091	0·8478	1·6956	0·05953	1·0140	2·0280
0·05164	0·7830	1·5660	0·05023	0·9493	1·8986
0·04234	0·7224	1·4448	0·04093	0·8826	1·7652
0·03258	0·7069	1·4138	0·03164	0·8160	1·6320
0·02326	0·6479	1·2958	0·02232	0·7537	1·5074
0·01441	0·5408	1·0816	0·01349	0·6406	1·2812
0·006506	0·3408	0·6816	0·006043	0·3913	0·7826

TABLE VI.

Sorption of aniline from 100 c.c. aqueous solution by 9·5 g. of resorcinol-formaldehyde resin.

C_e.	*x*.	*x*/*m*.	C_e.	*x*.	*x*/*m*.
0.1840	1·845	3·690	0·08768	1·348	2·696
0·1654	1·684	3·368	0·06890	1·191	2·382
0·1454	1·651	3·302	0·05065	1·000	2·000
0·1260	1·562	3·124	0·03200	0·08387	0·16774
0·1074	1·401	2·802	0·01523	0·04904	0·09808

It is clear from Table V that the hydroxides are adsorbed much more than the carbonates. The amount of adsorption of potassium hydroxide is practically the same as that of sodium hydroxide, while potassium carbonate is adsorbed to a greater extent than sodium carbonate.

Table VI shows the adsorption of aniline from aqueous solutions. It is obvious that the inorganic bases are adsorbed more than the organic bases.

(b) *Adsorption of Inorganic Acid.*—The adsorption of hydrochloric, sulphuric and nitric acids from aqueous solutions by an amino-resin has been studied and the results are shown in Table VII. The resin was prepared by condensing *m*-phenylenediamine (1 part), formaldehyde (2½ parts) and 50% hydrochloric acid (10 parts). The resin was dried in presence of hydrochloric acid and thoroughly washed with hot water to remove all impurities.

The results show that the inorganic acids are preferentially adsorbed in the order $H_2SO_4 > HNO_3 > HCl$. The adsorption of acids is, thus, influenced by their basicity and to a smaller degree by the nature of the anion.

TABLE VII.

Sorption of mineral acids from ·05*N* aqueous solutions by 0·5 g. of *m*-phenylene diamine-formaldehyde resin.

Sulphuric acid			Nitric acid			Hydrochloric acid		
C_e.	x.	x/m.	C_e.	x.	x/m.	C_e.	x.	x/m.
0·022020	1·2358	2·4716	0·03637	1·1070	2·2140	0·04077	1·002	2·0040
0·016614	1·1340	2·2680	0·02898	1·0010	2·0020	0·03232	0·9337	1·8674
0·011776	0·9980	1·9960	0·02159	0·8973	1·7946	0·02403	0·8565	1·7130
0·007388	0·8352	1·6704	0·01421	0·7914	1·5828	0·01658	0·7300	1·4600
0·003408	0·6480	1·2960	0·008097	0·6105	1·2210	0·009672	0·5689	1·1378
0·001163	0·3562	0·7124	0.002842	0·3782	0·7564	0·003452	0·3666	0·7332

SUMMARY AND CONCLUSIONS.

1. Synthetic resins have been prepared which show marked general adsorption.

2. The taking up of dissolved substances from solution by the adsorbent resins followed the ordinary laws of adsorption and is mainly a surface phenomenon as log x/m and log C_e curves are straight lines and x/m and C_e curves are typical adsorption isotherms.

3. A solute is apt to be weakly sorbed from solvents in which it is very soluble and from solvents possessing weak dipole moments. If the solubility of a given adsorbate is the same in a number of different solvents, greater adsorption will occur from solutions, the solvent of which has higher interfacial tension against the adsorbent.

4. The difference in degree of sorption from solvents may be used advantageously in the recovery of various substances from solutions.

5. Sorption of aromatic acids is greater than that of aliphatic acids.

6. In a homologous series, the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the series.

7. Effect of substituents on the sorptive affinity has been studied.

8. In the adsorption of inorganic bases, the hydroxides are adsorbed much more than the carbonates. The amount of adsorption of potassium hydroxide is practically the same as that of sodium hydroxide.

9. Inorganic acids are preferentially adsorbed in the order $H_2SO_4 > HNO_3 > HCl$.

10. The adsorptive resins resemble charcoal more than silica in their adsorptive properties. Silica adsorbs more from organic solutions than from aqueous solutions, while in the case of charcoal and the resins, it is quite the reverse. Further, whereas charcoal does not adsorb inorganic bases and silica inorganic acids, the adsorptive resins adsorb both types of substances fairly strongly.

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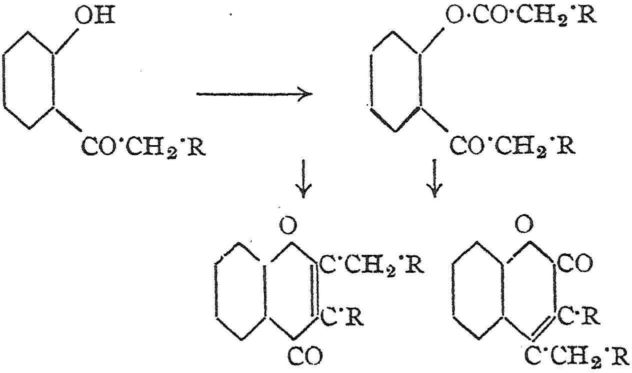
On the Limited Applicability of Kostanecki's Reaction.

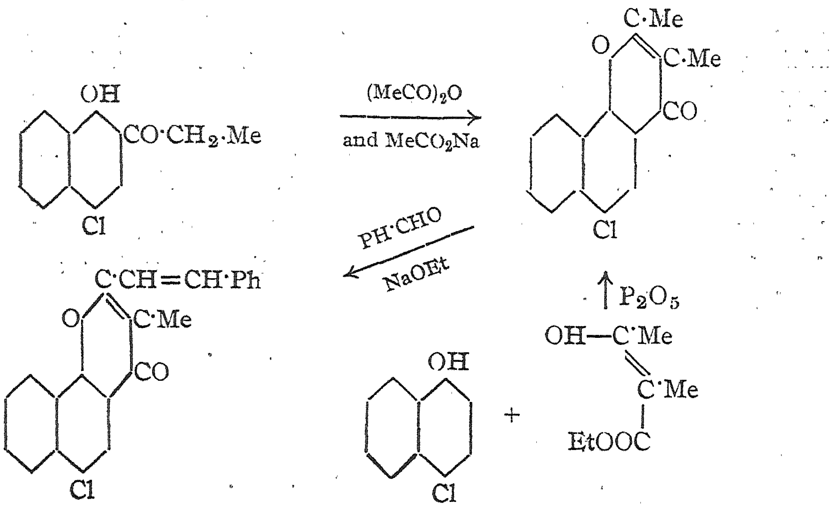
By Duhkhaharan Chakravarti and Phanindra Nath Bagchi.

In a series of papers Heilbron and his co-workers (*J. Chem. Soc.*, 1933, 1263; 1934, 1311, 1581; 1936, 296; *cf.* also Wittig, Baugert and Richter, *Annalen*, 1925, **446**, 155; Bargellini, *Atti. R. Accad. Lincei*, 1925, **2**, 261; Baker and Eastwood, *J. Chem. Soc.*, 1929, 2906; Chadha, Mahal and Venkataraman, *J. Chem. Soc.*, 1933, 1460; Flynn and Robertson, *ibid.*, 1936, 215) have shown that the course of Kostanecki's reaction is uncertain in as much as both coumarins and chromones are formed in this reaction (as in Simonis' reaction) and the reaction is dependent not only on the acid anhydrides and the salt used but also on the nature of the *o*-hydroxyphenylketone.

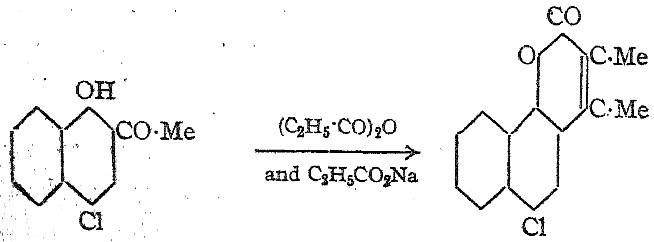


4-Chloro-2-aceto-1-naphthol and 4-chloro-2-propio-1-naphthol, prepared by heating the crude acetyl or propionyl derivative of 4-chloro-1-naphthol with aluminium chloride (Fries' rearrangement), have been submitted to Kostanecki's reaction with the typical acid anhydrides and their sodium salts, *e.g.*, (A) sodium acetate and acetic anhydride, (B) sodium propionate and propionic anhydride (C) sodium phenylacetate and phenylacetic anhydride, and (D) sodium benzoate and benzoic anhydride.

(A) On heating with sodium acetate and acetic anhydride both aceto- and propionaphthols give chromones and coumarins are not formed. In the case of 4-chloro-2-aceto-1-naphthol the 3-acetyl derivative of 6-chloro-2-methyl-1:4-$\alpha\beta$-naphthapyrone and in the case of 4-chloro-2-propio-1-naphthol, 6-chloro-2:3-dimethyl-1:4-αβ-naphthapyrone is formed, which is identical with the condensation product of 4-chloro-1-naphthol and methyl acetoacetic ester in presence of phosphorus pentoxide (Chakravarti and Bagchi, *J. Indian Chem. Soc.*, 1936, **13**, 649), as is shown by mixed melting point and the formation of identical benzylidene derivative.



(B) With sodium propionate and propionic anhydride, however, 4-chloro-2-aceto-1-naphthol gives a coumarin, *e.g.*, 6-chloro-3:4-dimethyl-1:2-αβ-naphthapyrone. It is identical, as proved by mixed melting point, with the product obtained by condensing 4-chloro-1-naphthol with methyl-acetoacetic ester using sulphuric acid as the condensing agent (Chakravarti and Bagchi, *loc. cit.*). 4-Chloro-2-propio-1-naphthol also gives a coumarin (6-chloro-3-methyl-4-ethyl-1:2-αβ-naphthapyrone) when heated with propionic anhydride and



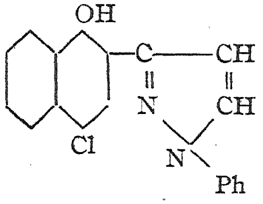
sodium propionate. This compound does not form a benzylidene derivative.

(C) Using phenylacetic anhydride and sodium phenylacetate, 4-chloro-2-aceto-1-naphthol yields 6-chloro-4-methyl-3-phenyl-1:2-αβ-naphthapyrone, which is identical with the condensation product of 4-chloro-1-naphthol and phenyl-acetoacetic ester using sulphuric acid as the condensing agent (Chakravarti and Bagchi, *loc. cit.*).

(D) When 4-chloro-2-aceto-1-naphthol is heated with benzoic anhydride and sodium benzoate, 6-chloro-2-phenyl-3-benzoyl-1:4-αβ-naphthapyrone is obtained as the main product, only traces of a second substance could be isolated which is probably the non-benzoylated 1:4-αβ-naphthapyrone.

The results obtained are, therefore, in agreement with the observations of Heilbron and co-workers (*loc. cit.*).

The simplest chromone from 4-chloro-2-aceto-1-naphthol, *e.g.*, 6-chloro-1:4-αβ-naphthapyrone has also been obtained by condensing it with ethyl formate in presence of molecular sodium. The intermediate hydroxymethylene-2-aceto-4-chloro-1-naphthol is a very stable compound and forms a characteristic green copper salt and yields a pyrazole derivative, 1-phenyl-3 (4′-chloro-1′-oxy-)-β-naphthylpyrazole with phenylhydrazine.



Various chalkones have been obtained by reacting 4-chloro-2-aceto-1-naphthol with different aldehydes, *e.g.*, benzaldehyde, anisaldehyde and veratric aldehyde. The insolubility of these chalkones in caustic alkalies and the fact that they are obtained as insoluble derivatives even in alkaline medium, when 4-chloro-2-aceto-1-naphthol is condensed with the aldehydes in presence of alcoholic sodium ethoxide led us to think that they are flavanone derivatives, but they do not respond to the colour test usually given by the flavanones (*cf.* Ashahina, Shinoda and Inubuse, *J. Pharm. Soc. Japan*, 1928, **48**, 208; Ashahina and Inubuse, *Ber.*, 1928, **61**, 1646 ; Kuroda, *J. Chem. Soc.*, 1930, 755). Attempts to prepare flavanones from these chalkones by boiling them with alcoholic sulphuric acid have not been successful, as pure products cannot be obtained.

4-Bromo-2-aceto-1-naphthol, prepared from 4-bromo-1-naphthol by Fries' rearrangement, is found to be identical with the compound obtained by Torry (*J. Amer. Chem. Soc.*, 1909, **31**, 1322) by bromination of 2-aceto-1-naphthol as is proved by the mixed melting point and the identical benzylidene derivative (m.p. 177°). Torry did not supply any definite evidence in favour of the assigned position of the bromine atom, but the present method of the preparation of the ketone from 4-bromo-1-naphthol leaves no doubt about the position of the bromine atom. Like acetochloronaphthol, 4-bromo-2-aceto-1-naphthol condenses with ethyl formate to give a stable hydroxymethylene compound which forms a pyrazole, *e.g.*, 1-phenyl-3-(4′-bromo-1′-oxy-)-β-naphthylpyrazole, with phenylhydrazine in acetic acid solution.

EXPERIMENTAL.

4-*Chloro*-2-*aceto*-1-*naphthol* (4-*chloro*-1-*oxy*-β-*naphthylmethyl ketone*).—Crude acetyl 4-chloro-1-naphthol, obtained from 4-chloro-1-naphthol (5 g.) and acetyl chloride (3·5 g.), was treated with finely powdered aluminium chloride (7 g.) and the mixture heated for 1½ hours on the water-bath. The cold mass was treated with ice and concentrated hydrochloric acid and again heated on a water-bath for 1 hour. The separated solid was collected, washed with water and crystallised as greenish needles from rectified spirit, m.p. 121°, yield 3·5 g. It gives a deep green colour with ferric chloride in alcoholic solution. It forms a very insoluble sodium salt and dissolves in concentrated sulphuric acid with a reddish brown colour. (Found : Cl, 16·24. $C_{12}H_9O_2Cl$ requires Cl, 16·10 per cent).

The *phenylhydrazone* crystallised from rectified spirit, m.p. 158-59°. (Found : N, 9·31. $C_{18}H_{15}ON_2Cl$ requires N, 9·01 per cent).

The *semicarbazone* crystallised from dilute acetic acid, it does not melt up to 275°.

The *methyl ether*, prepared by the action of dimethyl sulphate on an alkaline solution of the ketone, crystallised from methyl alcohol as yellowish needles, m.p. 66-67°. (Found : OMe, 12·61. $C_{13}H_{11}O_2Cl$ requires OMe, 13·22 per cent).

The *benzoyl* derivative crystallised from dilute alcohol, m.p. 123-24°. (Found : Cl, 11·32. $C_{19}H_{13}O_3Cl$ requires Cl, 10·94 per cent).

6-*Chloro*-2-*methyl*-3-*acetyl*-1 : 4-αβ-*naphthapyrone*.—A mixture of 4-chloro-2-aceto-1-naphthol (2 g.), acetic anhydride (8·5 g.) and freshly fused sodium acetate (3·5 g.) was heated at 130-140° for 2 hours. The temperature was raised in course of 3 hours to 160-170° which was maintained for 4 hours more. The reaction mixture was cooled, treated with water and heated on a water-bath for ½ hour and the solid was collected and extracted with alcohol. The alcoholic solution on cooling deposited a substance, m.p. 180-85°. On recrystallisation from glacial acetic acid almost colourless needles, m.p. 188-89°, were obtained. The substance, obtained from the acetic acid and alcohol mother-liquors by dilution with water, was subjected to repeated crystallisation from spirit but no second product could be isolated. (Found : C, 67·23 ; H, 3·85 ; Cl, 12·33. $C_{16}H_{11}O_3Cl$ requires C, 67·01 ; H, 3·84 ; Cl, 12·39 per cent).

6-Chloro-3 : 4-dimethyl-1 : 2-αβ-naphthapyrone.— A mixture of 4-chloro-2-aceto-1-naphthol (2 g.), propionic anhydride (6·5 g.) and sodium propionate (2·5 g.) was heated at 130-140° for 1 hour. The temperature was raised to 190° in course of 2 hours and it was heated at this temperature for 3 hours more. The tarry reaction product was heated with 10% sodium carbonate solution for ½ hour and the product washed with water and rectified spirit. It was finally extracted with boiling glacial acetic acid and the dirty substance, deposited on cooling, on repeated crystallisation from glacial acetic acid (charcoal) gave reddish needles, m.p. 202-3°, mixed m.p. with an authentic specimen of 6-chloro-3 :4-dimethyl-1 : 2-αβ-naphthapyrone, obtained by the condensation of 4-chloro-1-naphthol and methyl-acetoacetic ester with sulphuric acid as the condensing agent (Chakravarti and Bagchi, *loc. cit.*).

6-Chloro-2-phenyl-3-benzoyl-1 : 4-αβ-naphthapyrone.—A mixture of 4-chloro-2-aceto-1-naphthol (2 g.), benzoic anhydride (10 g.) and sodium benzoate (4 g.) was heated at 130-140° for 1½ hours and then at 190° for 6 hours. The mixture was heated on a water-bath for ½ hour with 10% sodium carbonate solution and the product crystallised from glacial acetic acid (charcoal) as yellow needles, m.p. 224°. (Found : Cl, 8·37. $C_{26}H_{15}O_3Cl$ requires Cl, 8·65 per cent).

The precipitate, obtained by diluting the acetic acid mother liquor, was extracted with rectified spirit and on cooling a substance, m.p. 210-15°, was obtained, but it did not depress the m.p. of 6-chloro-2-phenyl-3-benzoyl-1 : 4-αβ-naphthapyrone. The alcohol mother liquor on dilution gave a substance which after crystallisation from rectified spirit yielded a very small quantity of a substance, m.p. 152-54°, *6-Chloro-4-methyl-3-phenyl-1 : 2-αβ-naphthapyrone.*—4-Chloro-2-aceto-1-naphthol (2 g.), phenylacetic anhydride (8 g.) and sodium phenylacetate (2·5 g.) were heated at 130-40° for 1½ hours and then at 180° for 6 hours. The product, isolated in the usual manner, crystallised from glacial acetic acid (charcoal) as pale yellow needles, m.p. 215-16°, mixed m.p. with an authentic sample of 6-chloro-4-methyl-3-phenyl-1 : 2-αβ-naphthapyrone, obtained by the condensation of 4-chloro-1-naphthol and α-phenyl-acetoacetic ester (Chakravarti and Bagchi, *loc. cit*).

Hydroxymethylene-2-aceto-4-chloro-1-naphthol.—4-Chloro-2-aceto-1-naphthol (2·5 g.), suspended in dry formic ester (5·5 g.), was gradually added to a cold suspension of molecular sodium (1·5 g.) in dry ether (30 c.c.). The reaction set in after a few minutes and after keeping overnight the solution was treated with water, the ethereal layer was removed and the aqueous solution acidified. The yellow substance was collected and crystallised from rectified spirit as yellow amorphous powder, m.p. 146-47°. It gives a faint brown colour with ferric chloride and a green precipitate with copper acetate. (Found : Cl, 14·52. $C_{13}H_9O_3$ Cl requires Cl, 14·29 per cent).

1-Phenyl-3-(4′-chloro-1′-oxy-)-β-naphthylpyrazole was obtained by heating the above hydroxymethylene ketone with phenylhydrazine in glacial acetic acid solution on a water-bath for 2 hours. The solution on adding water deposited a red tarry mass, which was washed with dilute alcohol and finally crystallised from dilute acetic acid (charcoal) as yellow needles, m.p. 184°. (Found : N, 8·89. $C_{19}H_{13}ON_2Cl$ requires N, 8·74 per cent).

6-Chloro-1 : 4-αβ- naphthapyrone.—Hydroxymethylene-2 -aceto-4-chloro-1-naphthol (1 g.) was refluxed for 3 hours with sulphuric acid (*d* 1·84, 6 c.c.). The precipitate obtained on adding water to the alcoholic solution was crystallised twice from rectified spirit, m.p. 170-71°. (Found : C ; 67·41 ; H, 3·35. $C_{13}H_7O_2$ Cl requires C, 67·69 ; H, 3·04 per cent).

4-Chloro-2-propio-1-naphthol.—4-Chloro-1-naphthol (5 g.) and propionyl chloride (4·6 g.) were heated on a water-bath till there was no evolution of hydrochloric acid gas. Powdered aluminium chloride (7 g.) was added to the crude propionyl chloronaphthol and the mixture heated on a water-bath for 1½ hours. The cold mass was treated with powdered ice and the mixture heated on the water-bath for 1 hour with concentrated hydrochloric acid. The product was collected, washed with water and crystallised from rectified spirit as greenish needles, m.p. 90-91°, yield 4 g. It gives in alcoholic solution a deep green colour with ferric chloride. With caustic soda solution it forms an insoluble sodium salt and dissolves in concentrated sulphuric acid with a reddish-brown colour. (Found: Cl, 15·29. $C_{13}H_{11}O_2Cl$ requires Cl, 15·14 per cent).

The *semicarbazone*, crystallised from rectified spirit, did not melt up to 275°. (Found: N, 14·52. $C_{14}H_{14}O_2N_3Cl$ requires N, 14·41 per cent).

6-Chloro-2 : 3-dimethyl-1 : 4-αβ-naphthapyrone.—4-Chloro-2-propio-1-naphthol (2 g.), acetic anhydride (8·5 g.) and sodium acetate (3·5 g.) was heated at 130-40° for 1½ hours and then at 160-70° for 6 hours. The product, isolated in the usual manner, crystallised from dilute acetic acid (charcoal) as light yellow needles, m.p. 182-83°, mixed m.p. with an authentic sample of 6-chloro-2 : 3-dimethyl-1 : 4-αβ-naphthapyrone, obtained by the condensation of 4-chloro-1-naphthol with methyl-acetoacetic ester in presence of phosphorus pentoxide (Chakravarti and Bagchi, *loc. cit.*).

The precipitate, obtained by adding water to acetic acid mother-liquor, was subjected to repeated crystallisations but no other product could be isolated.

The *benzylidene* derivative, prepared by condensation with benzaldehyde in presence of alcoholic sodium ethoxide, melted at 189-90° and is identical with that prepared from 6-chloro-2 : 3-dimethyl-1 : 4-αβ-naphthapyrone.

6-Chloro-3-methyl-4-ethyl-1 : 2-αβ-naphthapyrone was prepared by heating 4-chloro-2-propio-1-naphthol (2 g.), propionic anhydride (6 g.) and sodium propionate (2·5 g.) at 130-40° for 1 hour and at 190° for 7 hours. The product, isolated in the usual manner, crystallised from alcohol (charcoal) as light yellow needles, m.p. 158-60°. No other product could be isolated. (Found: Cl, 12·76. $C_{16}H_{13}O_2Cl$ requires Cl, 13·02 per cent).

Attempts to condense the above compound with benzaldehyde to form the styryl derivative were unsuccessful.

4-Bromo-2-aceto-1-naphthol.—Powdered aluminium chloride (7 g.) was added to acetyl 4-bromo-1-naphthol, obtained from 4-bromo-1-naphthol (5 g.) and acetyl chloride (3 g.), and the mixture heated on a water-bath for 1 hour. The mixture was then treated with ice and heated on the water-bath with concentrated hydrochloric acid. The solid was collected, washed with water and crystallised from rectified spirit (charcoal) as greenish needles, m.p. 126-27°, mixed m.p. with the compound prepared by Torry (*loc. cit.*) by bromination of 2-aceto-1-naphthol. (Found : Br, 29·97. Calc. for $C_{12}H_9O_2Br$: Br, 30·19 per cent).

The *benzylidene* derivative, obtained by the condensation of the above ketone with benzaldehyde, crystallised from glacial acetic acid, m.p. 176-77° (*cf.* Torry, *loc. cit.*).

Hydroxymethylene-4-bromo-2-aceto-1-naphthol, prepared from 4-bromo-2-aceto-1-naphthol (2·5 g.), formic ester (5 c.c.) and molecular sodium (1·2 g.) in dry ether (30 c.c.), crystallised from alcohol, m. p. 147-48°. It gives a green precipitate with copper acetate solution. (Found : Br, 26·76. $C_{13}H_9O_3Br$ requires Br, 27·30 per cent).

1-Phenyl-3-(4′-bromo-1′- oxy-) - β - naphthylpyrazole, obtained by heating the above hydroxymethylene ketone with phenylhydrazine in glacial acetic acid solution, crystallised from alcohol (charcoal) as a yellow substance, m.p. 180-81°. (Found : N, 7·94. $C_{19}H_{13}ON_2Br$ requires N, 7·67 per cent).

Chalkones from 2-Aceto-4-chloro-1-naphthol.

Benzylidene-2-aceto-4-chloro-1-naphthol.—A solution of 4-chloro-2-aceto-1-naphthol (0·5 g.) in absolute alcohol was condensed with benzaldehyde (1 c. c.) in the presence of sodium ethoxide solution (0·2 g. of sodium in 25 c. c. of absolute alcohol) by heating on the water-bath for 20 minutes. The solution was diluted with water and the red precipitate was collected, washed with water and crystallised from glacial acetic acid, m. p. 186-87°. (Found : Cl, 11·0. $C_{19}H_{13}O_2$ Cl requires Cl, 11·50 per cent).

4′-Methoxy-benzylidene-2-aceto-4-chloro-1-naphthol, obtained by the condensation of 4-chloro-2-aceto-1-naphthol and anisaldehyde, crystallised from glacial acetic acid, m. p. 196-98°. (Found : Cl, 10·52. $C_{20}H_{15}O_3Cl$ requires Cl, 10·49 per cent).

3′:4′-Dimethoxybenzylidene-2-aceto-4-chloro-1-naphthol, the condensation product of 2-aceto-4-chloro-1-naphthol and veratric aldehyde, crystallised from dilute acetic acid, m. p. 174-76°. (Found : Cl, 10·10. $C_{21}H_{17}O_4$ Cl requires Cl, 9·63 per cent).

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The Action of Hydrogen Sulphide on Mercurous Chromate.

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The reduction of chromates by hydrogen sulphide has been investigated by Dunnicliff and co-workers (*J. Phys. Chem.*, 1929, **33**, 81 ; 1930, **35**, 3214 ; 1935, **39**, 1217 ; *J. Indian Chem. Soc.*, 1935, **12**, 595).

Dunnicliff and Prakash (*J. Indian Chem. Soc.*, 1935, **12**, 505,) have shown that silver chromate, when reduced with hydrogen sulphide, yields sulphite as one of the final products. It has been pointed out that silver chromate is one of those substances which are not hydrolysed to any extent by water. Further support of this view has been obtained in the action of hydrogen sulphide on mercurous chromate, a substance which is hydrolysed only at temperatures about 60°. The effect of temperature on the products formed is also emphasised.

For the purpose of this work, mercurous chromate was obtained by mixing approximately equivalent proportions of potassium chromate and mercurous nitrate. The basic mercurous chromate which separated was converted into the normal compound by boiling with a few drops of concentrated nitric acid and washing till free from acid.

The reaction was studied at three temperatures :

I. *At room temperature.* A known weight of the sample when subjected to the action of hydrogen sulphide at the room temperature (about 20°), gave an orange-red suspension which changed ultimately to dull black. After 8 hours, about 50% of the mercurous chromate had been attacked. Sulphite, thiosulphate and sulphate were absent from the filtrate. On extraction with potassium hydroxide, the precipitate was found to contain thiosulphate, sulphite and sulphate. The residue was chromium hydroxide, mercurous sulphide and free sulphur.

II. *At* 80-85°. A known weight was suspended in water and treated as before, the reaction being maintained at 80-85° in a water bath. The final reaction mixture was black in colour but there was no *sulphite* in the alkali extract. Other products were the same as before.

III. *At about* 0°. The vessel was placed in melting ice. The products were the same as at the room temperature, except that, for a given weight of mercurous chromate, more of the sulphite was formed. This has an important bearing on the subject.

For purposes of quantitative relations, the following reactions are assumed :

$$Hg_2CrO_4 + H_2S \rightarrow Hg_2S + H_2CrO_4$$
$$H_2CrO_4 \rightarrow CrO_3 + H_2O.$$

(*i*) $3H_2S + 8CrO_3 \rightarrow Cr_2\,(SO_4)_3H + 3_2O + 3Cr_2O_3.$
36 g. $(SO_4)'' \equiv 517·22$ g. Hg_2CrO_4.

(*ii*) $8CrO_3 \rightarrow 4Cr_2O_3 + 12(O)$
$6H_2S + 12(O) \longrightarrow 3H_2S_2O_3 + 3H_2O$
42 g. $(S_2O_3)'' \equiv 517·22$ g. Hg_2CrO_4.

(*iii*) $2\,CrO_3 \rightarrow Cr_2O_3 + 3\,(O)$
$H_2S + 3(O) \rightarrow H_2SO_3.$
40 g. $(SO_3)'' \equiv 517·22$ g. Hg_2CrO_4.

(*iv*) $2CrO_3 + 3H_2S \longrightarrow Cr_2O_3 + 3H_2O + 3S$
48 g. sulphur $\equiv 517·22$ g. Hg_2CrO_4.

TABLE I.

The action of hydrogen sulphide on mercurous chromate in ice-cold solutions.

Analysis of the final greenish black precipitate.

	I.	II.	III.	Mean
1. Sulphite $(SO_3)''$				
(*a*) Actual wt. 100/*x**	0·543 g.	0·482 g.	0·573 g.	0·533 g.
(*b*) In terms of 100 g. of Hg_2CrO_4.				6·88%
2. Thiosulphate $(S_2O_3)''$				
(*a*) Actual wt. 100/*x**	3·194	3·040	3·437	3·224
(*b*) In terms of 100 g. of Hg_2CrO_4.				39·67%
3. Sulphate $(SO_4)''$				
(*a*) Actual wt. 100/*x**	1·251	1·096	1·192	1·180
(*b*) In terms of 100 g. of $Hg_2\,CrO_4$.				16·95%
4. Sulphur				
(*a*) Actual wt. 100/*x**	3·27	3·70	3·96	3·64
(*b*) In terms of 100 g. of $Hg_2\,CrO_4$.				39·22%

Total mercurous chromate accounted for = 102·72

* Where *x* is the percentage of mercurous chromate actually attacked.

TABLE II.

The action of hydrogen sulphide on mercurous chromate at 80-85°.

	I.	II.	III.	Mean.
1. Sulphite $(SO_3)''$	...	...	...	Absent
2. Thiosulphate (S_2O_3)				
(*a*) Actual wt. 100/*x**	3·129 g.	3·547 g.	3·276 g.	3·317 g.
(*b*) In terms of 100 g. of $Hg_2 CrO_4$.				40·85%
3. Sulphate $(SO_4)''$				
(*a*) Actual wt. 100/*x**	1·455	1·234	1·521	1·403
(*b*) In terms of 100 g. of Hg_2CrO_4.				20·16%
4. Sulphur				
(*a*) Actual wt. 100/*x**	3·65	4·21	3·89	3·92
(*b*) In terms of 100 g. of $Hg_2 CrO_4$.				42·25%

Total mercurous chromate accounted for = 103·26

In view of the fact that the gas had to be passed for about 8 hours, the high values of sulphur are attributable to the adventitious oxidation of hydrogen sulphide.

The total oxidising power of the chromate has been accounted for in terms of the products formed.

The results show that, when the reaction is conducted in ice-cold solutions, the final precipitate contains chromium sulphate, thiosulphate, sulphite and hydroxide, mercurous sulphide and free sulphur. At temperatures above 60°, *i.e.*, when hydrolysis occurs, sulphite is absent and the analytical results show that it is quantitatively converted into sulphate, since the values for thiosulphate are practically the same as at the lower temperature. It appears, therefore, that in the event of hydrolysis, sulphite is converted quantitatively into sulphate. Thallous chromate is not hydrolysed by water and also gives sulphite among the reduction products.

Similar experiments with barium chromate and chromic acid have shown that at 80-85°, the products show an increase in the sulphate content and decrease in the value for thiosulphate, although no sulphite appears in the final products. High temperatures, therefore, favour the reaction $SO_3 + O \longrightarrow SO_4$ in preference to $SO_3 + S \longrightarrow S_2O_3$.

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* Where *x* is the percentage of mercurous chromate actually attacked.

On some Synthetic Compounds related to Atophan.

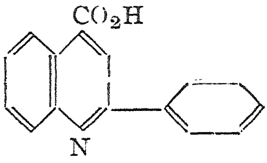
By Prafulla Kumar Bose and Nirmal Chandra Guha.

2-Phenylquinoline-4-carboxylic acid (I, known under the trade name of 'Atophan' and 'Cinchophen') is a valuable synthetic drug. It possesses antipyretic as also antiphlogistic action, but the most important physiological property of the drug is the uricosuric action and hence its administration in the treatment of gout or rheumatism. It is, however, not a harmless substance as is generally supposed and indiscriminate use, even in clinical doses, has resulted in many fatal accidents, the victims developing gastro-intestinal disturbances and jaundice sooner or later. Attempts have been made to modify the structure of atophan with a view to diminish its undesirable pathological reactions on the liver, but satisfactory results have so far not been obtained. The modified atophans may be classified as follows :

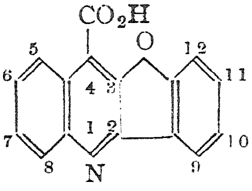
(*i*) Esters of atophan.
(*ii*) Atophan derivatives having substituents in the phenyl nucleus in position 2.
(*iii*) Atophan derivatives having substituents in the benzene nucleus of the quinoline ring.

A study of the chemical constitution and uricosuric action of these and allied compounds shows that a phenyl group in position-2 and a carboxyl group in position 4 of the quinoline nucleus are essential for the uricosuric action. Substituents [such as OH, Me, OMe, Ph, CO_2H, $-O-CH_2-O-$, As: $O(OH)_2$] attached to the phenyl group or the pyridine ring do not improve the quality of the drug, but have on the contrary often harmful effects (Niccolaier and Dohrn, *Deut. Arch. klin. Med.*, 1908, **93**, 331 ; Dohrn, *Münch. med. Wochenschr.*, 1912, **59**, 568 ; *Biochem. Z.*, 1912, **43**, 240 ; *Z. klin. Med.*, 1912, **74**, 444 ; Impens, *Arch. intern. Pharmakodyn.*, 1912, **22**, 379). Introduction of substituents in the benzene nucleus has no harmful effect but it often, though not always, reduces or suppresses the uricosuric action. Similar results are obtained when the CO_2H group of atophan is esterified or converted into an amide.

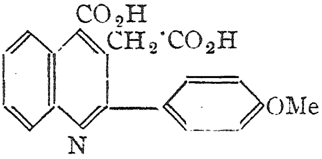
The present investigation was undertaken with a view to prepare compounds of the type (II) and study their physiological action. An inspection of the formula shows that it satisfies the two fundamental conditions necessary for uricosuric action, namely a phenyl group in position 2 and a carboxyl in position 4. Moreover, interposed between the phenyl and the quinoline nuclei there is a furan ring which is likely to influence the physiological activity of the compounds. The substances have been prepared by condensing isatin with relevant coumaranones in alkaline medium. Incidentally the compounds III—V have been prepared from isatin on the one hand and β-anisoylpropionic acid, α-naphthylmethylketone and β-naphthylmethylketone on the other. The physiological action of these complex furoquinolines will be investigated.



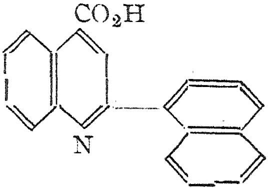
(I)



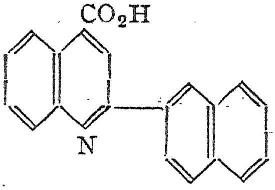
(II)



(III)



(IV)



(V)

EXPERIMENTAL.

Preparation of Coumaranones.—Coumaranones were prepared by Mameli's method (*Gazzetta*, 1926, **56**, 759) which was found to give better yields than the methods of Störmer and Bartsch (*Ber.*, 1900, **33**, 3177) or Störmer and Atenstadt (*Ber.*, 1902, **35**, 3569).

Methylcoumaranones were prepared by the method of Higginbotham and Stephen (*J. Chem. Soc.*, 1920, **117**, 1534) and 6-oxycoumaranone by the method of Arima and Okamato (*J. Chem. Soc. Japan*, 1929, **50**, 344).

Condensation of Coumaranones with Isatic Acid.—One mol. of isatin was boiled with an excess of alcoholic potassium hydroxide for 20 mins. One mol. of coumaranone was then added and the mixture kept at about 70° for 3—4 hours. The solution was then made just acidic with dilute hydrochloric acid and the yellow precipitate collected. The acids were purified through the sodium salts. For this purpose the acids were dissolved in dilute sodium carbonate solution avoiding excess, charcoaled and filtered and the filtrate concentrated. The sodium salts were collected and decomposed with dilute hydrochloric acid. The precipitate was thoroughly washed with water, alcohol and finally with acetone. The yields were generally good. The compounds formed cream-coloured microcrystalline substances, sparingly soluble in acids but easily in sodium bicarbonate solutions. Condensations with β-anisoylpropionic acid and the naphthylmethylketones were similarly carried out. The following table summarises the analytical and other data of the compounds.

Compounds.	M. p.	Yield.	Analytical data.	
			Found.	Calc.
2 :3-Benzofuroquinoline-4-carboxylic acid, $C_{16}H_9O_3N$, from coumaranone (II)	277°	81%	*C, 72·68 % 72·68 H, 3·09 3·49 N, 5·44	73·00% 3·42 5·32
,, Sodium salt, $C_{16}H_8O_3NNa$.	—	—	Na, 7·91	8·07
2 : 3 - (12-Methyl-) benzofuroquinoline-4 carboxylic acid, $C_{17}H_{11}O_3N$, from 7-methylcoumaranone.	286°	64	C, 73·53 H, 4·22	73·64 3·97
,, Sodium salt $C_{17}H_{10}O_3NNa, 2H_2O$.	—	—	Na, 6·76 H_2O, 10·74	6·87 10·75
2 : 3 - (11-Methyl-) benzofuroquinoline-4-carboxylic acid, $C_{17}H_{11}O_3N$, from 6-methylcoumaranone.	281°	80	C, 73·18 H, 4·17 N, 4·86	73·64 3·97 5·05
,, Sodium salt, $C_{17}H_{10}O_3NNa$.	—	—	Na, 7·45	7·69

Compounds.	M.p.	Yield.	Analytical data. Found.	 Calc.
2 : 3 - (10-Methyl-) benzofuroquinoline-4-carboxylic acid, $C_7H_{11}O_3N$ from 5-methylcoumaranone.	275°	50%	C, 73·52% H, 4·11	73·64% 3·97
2 : 3-(11-Hydroxy-) benzofuroquinoline-4-carboxylic acid, $C_{16}H_9O_4N$, from 6-hydroxycoumaranone.	309°	70	C, 68·74, 68·79 H, 3·46, 3·44 N, 4·93	68·82 3·23 5·02
2-*p*-Anisylquinoline-4-carboxylic-3-acetic acid (III), $C_{19}H_{15}O_5N$ from $MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.	273° (reddish at 210°)	66	C, 67·61 H, 4·55 N, 3·86	67·66 4·45 4·16
2-α-Naphthylquinoline-4-carboxylic acid (IV), $C_{20}H_{13}O_2N$, from methyl-α-naphthyl-ketone.	195-97°	79	C, 79·87 H, 4·50 N, 4·54	80·26 4·35 4·68
2-β-Naphthylquinoline-4-carboxylic acid (V). $C_{20}H_{13}O_2N$, from methyl-β-naphthyl ketone.	248°	90	C, 79·91 H, 4·65 N, 4·62	80·26 4·35 4·68
" Sodium salt, $C_{20}H_{12}O_2NNa$	—	—	Na, 7·06	7·16

* All the C-H estimations were carried out by ter Meulen's semi-micro method. Samples were dried at 110° in vacuum before analysis.

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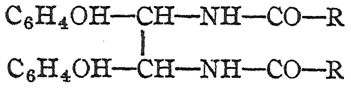
Condensations of Furil and Furoin.

By Anukul Chandra Sircar and Sudhangsu Chandra Guha.

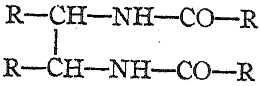
The remarkable resemblance between benzaldehyde and furfural is further exemplified by great similarity in the chemical behaviour of benzoin and furoin as well as benzil and furil, both of which undergo exactly similar types of condensations. Thus it has been found that just like benzil furil undergoes the following condensations:

(1) Furil condenses with aldehydes in presence of ammonia forming iminazoles (*cf.* Japp and co-workers, *J. Chem. Soc.*, 1882, **41**, 326; 1883, **43**, 10; 1884, **45**, 672, *et al*) and no oxazoles could be isolated though the condensations were effected at different temperatures and pressures (*cf.* Sircar and Guha-Roy, *J. Chem. Soc.*, 1925, **127**, 1048; Sircar and Sen, *J. Indian Chem. Soc.*, 1936, **13**, 482). Furil condenses with salicylaldehyde and furfuraldehyde forming compounds (I) and (II) (*cf.* Japp, *J. Chem. Soc.*, 1884, **45**, 672).



$$\begin{array}{l} C_6H_4OH\text{—}CH\text{—}NH\text{—}CO\text{—}R \\ \qquad\qquad\;\; | \\ C_6H_4OH\text{—}CH\text{—}NH\text{—}CO\text{—}R \end{array}$$

(I)



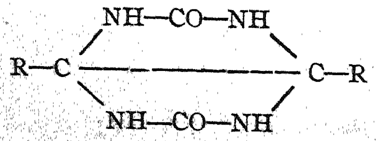
$$\begin{array}{l} R\text{—}CH\text{—}NH\text{—}CO\text{—}R \\ \qquad | \\ R\text{—}CH\text{—}NH\text{—}CO\text{—}R \end{array}$$

(II)

$[R=C_4H_3O]$

(2) Furil reacts with compounds containing reactive methylene groups, *e.g.*, acetoacetic ester, cyanoacetic ester, benzyl cyanide, acetylacetone, malonic ester, phloroglucinol, hippuric acid using piperidine as the condensing agent. In each case only one of the ketonic groups of furil reacts with one molecule of the compound containing reactive methylene group, while Japp and Lander (*J. Chem. Soc.*, 1896, **69**, 736), observed that one molecule of acetoacetic ester condenses with two molecules of benzil.

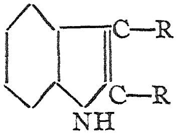
(3) Furil condenses with urea and thiourea with the formation of ureine (III) and thioureine (*cf.* Anschutz and Geldermann, *Annalen*, 1891, **261**, 129).

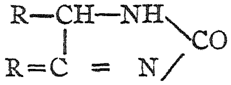


$(R=C_4H_3O)$

(III)

Similarly like benzoin furoin also undergoes condensations with (*a*) primary monoamines forming indoles (IV) (*cf.* Japp and Murray, *J. Chem. Soc.*, 1894, **65**, 889)





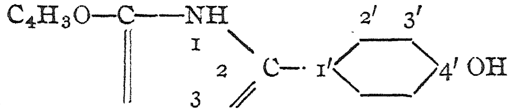
(R = C_4H_3O) (V)

(IV)

(*b*) urea and thiourea forming iminazolone (V) and thioiminazolone.

EXPERIMENTAL.

4'-Hydroxy-2-phenylfuriliminazole.



(VI)

Furil (0·5 g.) and *p*-hydroxy-benzaldehyde (0·36 g.) were heated with excess of liquor ammonia in a sealed tube at 165° for 1½ hours. The resulting precipitate was washed with alcohol and crystallised from nitrobenzene in greyish-white microscopic plates, m.p. 235-36°. It is soluble in acetic acid and nitrobenzene; insoluble in ether, benzene, alcohol, acetone, chloroform and carbon tetrachloride. It dissolves in sulphuric acid with a brown colour and in boiling caustic alkalies. (Found : N, 9·7. $C_{17}H_{12}O_3N_2$ requires N, 9·6 per cent).

3'-Hydroxy-2-phenylfuriliminazole was prepared in the same way as the preceding compound from furil (0·5 g.) and *m*-hydroxybenzaldehyde (0·36 g.). It crystallised from nitrobenzene in white microscopic plates, m.p. 265° (with previous blackening at 225°). It is soluble in chloroform, acetone and alcohol. (Found : N, 9·1. $C_{17}H_{12}O_3N_2$ requires N, 9·6 per cent).

4'-Nitro-2-phenylfuriliminazole was prepared as usual from furil (1 g.) and *p*-nitrobenzaldehyde (0·36 g.). It separated from acetone in yellow microscopic plates, m.p. 175° (with blackening at 170°). It is insoluble in ether, benzene and carbon tetrachloride, and soluble in chloroform and nitrobenzene. It dissolves in dilute acetic acid with a beautiful yellow colour. (Found: N, 13·5. $C_{17}H_{11}O_4N_3$ requires N, 13·1 per cent).

Condensation of Furil with Salicylaldehyde.—Through an absolute alcoholic solution of furil (1 mol., 1·3 g.) and salicylaldehyde (2 mols., 1·8 g.) dry ammonia gas was passed until the solution was saturated. The flask was then corked and allowed to stand for 1 hour. The separated lemon-yellow rectangular crystals were filtered and repeatedly washed with hot alcohol. It is insoluble in ether, alcohol, chloroform, carbon tetrachloride, acetic acid and nitrobenzene and soluble in pyridine. It does not melt up to 307°. It dissolves in caustic potash solution on long boiling, and is reprecipitated on the addition of acids. (Found: N, 7·0. $C_{24}H_{20}O_6N_2$ requires N, 6·5 per cent).

The *acetyl* derivative was prepared by heating it with 3 times its weight of acetic anhydride for 3 hours and was obtained as transparent rectangular plates, m.p. 246°. (Found: N, 5·8. $C_{28}H_{24}O_8N_2$ requires N, 5·4 per cent).

Condensation of Furil with Furfuraldehyde.—Dry ammonia gas was passed through the solution of furil (1 mol., 0·8 g.) and furfuraldehyde (0·9 g.) in hot absolute alcohol till it was saturated and the mixture allowed to stand overnight. The separated yellow needles were collected and washed with hot alcohol. It does not melt up to 280°. It is insoluble in any of the common organic solvents except pyridine and resembles the preceding compound in its properties. (Found: N, 7·6. $C_{20}H_{16}O_6N_2$ requires N, 7·3 per cent).

Phenylcyanoethylene-desoxyfuroin.—A mixture of furil (1·5 g.), benzyl cyanide (1 g.), piperidine (0·5 c.c.) and absolute alcohol (50 c.c.) was heated on the water-bath for 7 hours under reflux. The mixture, diluted with water, was mixed with sodium acetate (2 g.) when a crystalline precipitate separated. This was collected, washed with water and finally crystallised from alcohol as brown microscopic plates, not melting up to 275°. It is soluble in acetone, acetic acid and chloroform but insoluble in ether and benzene. (Found: N, 4·99. $C_{18}H_{11}O_3N$ requires N, 4·8 per cent).

Benzoylaminocarboxyethylene-desoxyfuroin was prepared in the same way as the preceding compound from furil (1·5 g.) and hippuric acid (1·4 g.). It crystallised from alcohol in dark grey microscopic plates, not melting up to 265°. It is soluble in acetone, chloroform and nitrobenzene but insoluble in ether. (Found: N, 3·97. $C_{19}H_{13}O_6N$ requires N, 3·9 per cent).

Cyanocarbethoxyethylene-desoxyfuroin was prepared in the same way as the preceding compounds from furil (1·5 g.) and ethyl cyanoacetate (0·9 g.). It crystallises from acetone in brown microscopic plates, not melting up to 255°. It is insoluble in ether but soluble in alcohol and chloroform. (Found: N, 5·11. $C_{15}H_{11}O_5N$ requires N, 4·9 per cent).

Acetylcarbethoxyethylene-desoxyfuroin, prepared from furil (1·5 g.) and ethyl acetoacetate (1·2 g.), was obtained as brown microscopic plates from alcohol, not melting up to 275°. It is soluble in acetic acid, acetone and chloroform but insoluble in benzene and ether. (Found: C, 64·0; H, 4·2. $C_{16}H_{14}O_6$ requires C, 63·2; H, 4·6 per cent).

Dicarbethoxyethylene-desoxyfuroin, prepared from furil (1·5 g.) and ethyl malonate (1·3 g.), crystallised from alcohol in brown microscopic plates. It resembles the foregoing compounds in its properties. (Found: C, 62·2; H, 4·1. $C_{17}H_{16}O_7$ requires C, 61·4; H, 4·7 per cent).

Diacetylethylene-desoxyfuroin, prepared from furil (1·5 g.) and acetylacetone (0·8 g.), crystallised from alcohol in brown microscopic plates not melting up to 258°. It is soluble in acetone but insoluble in ether and benzene. (Found: C, 66·8; H, 4·01. $C_{15}H_{12}O_5$ requires C, 66·1; H, 4·4 per cent).

The condensation product of furil (1·5 g.) and phloroglucinol (1 g.) crystallised from acetone as brown microscopic plates, not melting up to 272°. (Found: C, 65·0; H, 3·2. $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·3 per cent).

Furil Diureine.—The fused mass, obtained by heating an intimate mixture of furil (1 g.) and urea (3 g.) at 200° was repeatedly boiled with alcohol to remove any unreacted urea. It was obtained as a brown crystalline powder not melting up to 295°. It dissolves in sulphuric acid and glacial acetic acid with a black colour. (Found: N, 20·7. $C_{12}H_{10}O_4N_4$ requires N, 20·4 per cent).

Furil Dithioureine, prepared from furil (0·8 g.) and thiourea (2·1 g.) exactly in the same way as in the previous compound, was obtained as a brown crystalline powder, not melting up to 300°. It is insoluble in all the common organic solvents and resembles the previous compound in its properties. (Found: N, 18·3. $C_{12}H_{10}O_2N_4S_2$ requires N, 18·3 per cent).

4:5-*Difuryl-2-iminazolone.*—An alcoholic solution of furoin (1·7 g.) and urea (0·6 g.) was heated in a sealed tube at 165° for 3 hours. The resultant precipitate was washed repeatedly with boiling alcohol when it was obtained as a brown crystalline powder. It is insoluble in the common organic solvents and does not melt up to 290°. (Found: N, 13·5. $C_{11}H_8O_3N_2$ requires N, 12·9 per cent).

4:5-*Difurylthioiminazolone.*—It was prepared in the same way as the preceding compound from furoin (1 g.) and thiourea (0·4 g.) and was obtained as a crystalline powder. (Found: N, 12·7. $C_{11}H_8O_2N_2S$ requires N, 12·06 per cent).

2′:3′-*Difurylindole.*—An intimate mixture of furoin (2·4 g.), aniline (4 g.) and aniline hydrochloride (1·6 g.) was heated on the oil-bath for 2½ hours in such a way that the water formed during the reaction could escape but any aniline evaporating flowed back. It was finally washed with water and crystallised from dilute pyridine in brown microscopic plates, not melting up to 285°. (Found: N, 5·8. $C_{16}H_{11}O_2N$ requires N, 5·6 per cent).

2′:3′-*Difuryl*-o-*toluindole* was prepared from furoin (1·8 g.), *o*-toluidine (2 g.) and *o*-toluidine hydrochloride (0·8 g.) in the same way as the above compound. It is soluble in hot acetone from which it separates in the form of brown microscopic plates, m.p. 201-3°. (Found: N, 5·2. $C_{17}H_{13}O_2N$ requires N, 5·3 per cent).

2′:3′-*Difuryl*-p-*toluindole.*—The viscous mass obtained by keeping an intimate mixture of furoin (1·5 g.), *p*-toluidine (2 g.) and *p*-toluidine hydrochloride (0·6 g.) in a well-corked flask for 2 days, was heated for 1½ hours at 160°. The resultant precipitate was digested with dilute hydrochloric acid and finally washed with water. It separates from acetone in brown microscopic plates, m.p. 210° (blackening at 180°). It dissolves in alcohol, chloroform and nitrobenzene. (Found: N, 5·6. $C_{17}H_{13}O_2N$ requires N, 5·3 per cent).

2′:3′-*Difuryl-β-naphthindole.*—Furoin (1·6 g.), *β*-naphthylamine (2 g.) and *β*-naphthylamine hydrochloride (0·8 g.) were heated at 175° for 3 hours. The product was digested with dilute hydrochloric acid, washed with water and finally crystallised from acetone in dark brown microscopic plates, m.p. 184-85° (darkening at 170°). It dissolves in alcohol and nitrobenzene. (Found: N, 5·01. $C_{20}H_{13}O_2N$ requires N, 4·6 per cent).

2′:3′-*Difuryl-α-naphthindole* was prepared in the same way from furoin (1·6 g.), α-naphthylamine (2 g.) and α-naphthylamine hydrochloride (0·8 g.). It crystallises from acetone in brown microscopic plates, not melting up to 240° after which it decomposes. (Found: N, 5·0. $C_{20}H_{13}O_2N$ requires N, 4·6 per cent).

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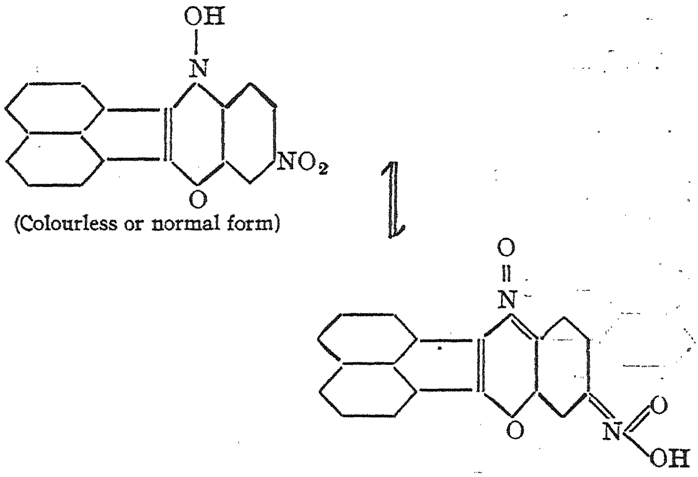
Studies in Acenaphthenequinone Series. Part III.

By Anukul Chandra Sircar and Dwipendra Chandra Chowdhury.

In most of the condensation reactions, acenaphthenequinone behaves like phenanthraquinone and yields similar products (*cf.* Sircar and Guha, *J. Chem. Soc.*, 1924, **125**, 335 ; Guha, *ibid.*, 1931, **139**, 582 ; Sircar and Guha-Ray, *J. Indian Chem. Soc.*, 1929, **6**, 93). The present investigation is only an extension of the reactions already studied by one of the present authors.

(A) *o*-Aminophenol and its derivatives (*cf.* Kehrmann, *Ber.*, 1905, **33**, 2952) condense with acenaphthenequinone forming the ψ-bases acenaphthaphenazoxines. Hydroxy-acenaphtha- 5- nitrophenazoxine, obtained by the condensation of acenaphthenequinone with 5-nitro-2-aminophenol, has been obtained in two varieties having identical m.p. (186°) but differing in colour and crystalline shapes. The azoxine, therefore, exhibits chromoisomerism.

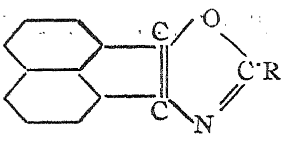


(Colourless or normal form)

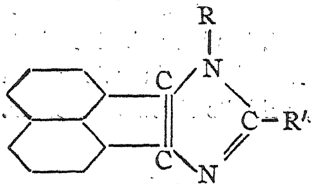
(Coloured or aci form)

The hydroxy-acenaphthaphenazoxines dissolve readily in strong sulphuric acid and on allowing the solution to stand for some time a highly coloured substance separates, which might be either the sulphate or the unstable ψ-base. When the sulphuric acid solution is diluted with water, acenaphthenequinone is precipitated. The phenazoxines when boiled for a few minutes with dilute hydrochloric acid undergo similar decomposition. It is also interesting to note that the phenazoxines when brominated or reduced with stannous chloride (*cf.* Kehrmann, *loc. cit.*), break up regenerating acenaphthenequinone. Evidently the hydroxyacenaphthaphenazoxines are more unstable when compared with the hydroxyphananthraphenazoxines. In attempting to reduce the phenazoxines by phenylhydrazine according to the method of Kehrmann, products are obtained in which the percentage of nitrogen is much greater than that required by the formula of the above author and corresponds with that of the compounds in which one of the oxygen atoms is as if replaced by nitrogen.

(B) Acenaphthenequinone has been condensed with primary amines forming iminazoles and oxazoles (*cf.* Japp and Davidson, *J. Chem. Soc.*, 1895, **67**, 32).

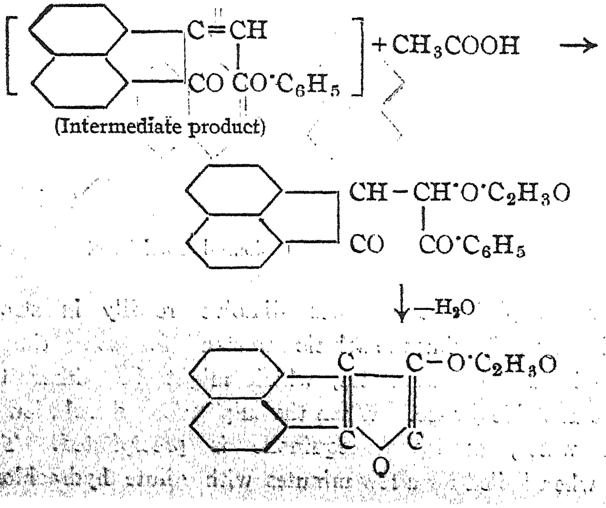


(R=H, Ph, Me)



(R=CH_2Ph, Me, Et; R′=Ph, H, Me respectively).

(C) Acetophenone has been condensed with acenaphthenequinone in presence of acetic anhydride forming 3-acetoxy-2-phenyl-4:5-acenaphthylenefuran (*cf.* Japp and Wood, *J. Chem. Soc.*, 1905, **87**, 712).



(D) The condensation of acenaphthenequinone with acetic anhydride in presence of anhydrous sodium acetate leads to the formation of two distinct compounds (*cf.* Schwarin, *Ber.*, 1905, 38, 1270) having empirical formulæ $C_{13}H_6O_2$ (green) and C_5H_3O (red). The green compound when heated with potash yields an acid (empirical formula C_5H_3O). The red substance when boiled with potash also yields an acid, identical with the condensation product of acenaphthenequinone with glycollic acid.

(E) Alcoholic caustic potash reacts with acenaphthenequinone (*cf.* Mayer and Spengler, *Ber.*, 1905, 38, 440) forming naphthalic anhydride and the lactone of 8-hydroxyacenaphthyl-7-glyoxylic acid.

In all the studied chemical reactions, therefore, acenaphthenequinone behaves exactly like phenanthraquinone although differing widely from the latter in constitution.

EXPERIMENTAL.

Hydroxy-acenaphthaphenazoxine.—A mixture of acenaphthenequinone (2·5 g.), *o*-aminophenol (1·5 g.) and benzene (30 c.c.) was heated for about 45 minutes, and the solution filtered hot. The deep brown crystals separating were recrystallised from a mixture of benzene and alcohol (1:1) in cubes, m.p. 187° (decomp.). It is sparingly soluble in benzene and water, moderately soluble in nitrobenzene and chloroform. It dissolves in concentrated sulphuric acid with a deep brown colour (green fluorescence) and on addition of water yellowish brown precipitate is obtained which is identified to be acenaphthenequinone. (Found : N, 5·05. $C_{18}H_{11}O_2N$ requires N, 5·13 per cent).

Attempts to reduce the ψ-base with stannous chloride and hydrochloric acld (*cf.* Kehrmann, *loc. cit.*) lead to the decomposition of the ψ-base and acenaphthenequinone is identified as one of the products of decomposition.

Action of Bromine.—The ψ-base (1 g.), dissolved in warm nitrobenzene (10 g.), was treated with a solution of bromine in nitrobenzene (14 g., 10%). After about 10 minutes on the addition of about 5 times the volume of ether, a precipitate separated which after crystallisation from acetic acid was identified to be acenaphthenequinone.

Action of Phenylhydrazine.—The ψ-base was rubbed to a paste with excess of phenylhydrazine and carefully warmed, when a solution was obtained which soon solidified. The solid mass was repeatedly washed with alcohol and repeatedly crystallised from a mixture of benzene and alcohol as orange needles, m. p. 175°. (Found : N, 9·9). The percentage of nitrogen should be exactly half, if the reduction proceeds in the way indicated by Kehrmann (*loc. cit.*).

Hydroxy-acenaphtha-5-nitrophenazoxine.— Acenaphthenequinone (4 g.), 5-nitro-2-aminophenol (3·5 g.) and benzene (150 c.c.) were heated for 2 hours, when a dirty white substance separated. It was filtered and crystallised from alcohol in yellowish orange thick plates, m.p. 186° (decomp.). It is almost insoluble in benzene, but very soluble in alcohol (a deep red colour). (Found : N, 8·43. $C_{18}H_{10}O_4N_2$ requires N, 8·8 per cent). When crystallised from xylene it separates as white needles, m.p. 186° (decomp.). (Found : N, 8·8. $C_{18}H_{10}O_4N_2$ requires N, 8·8 per cent).

The colourless variety dissolves in alcohol to a red solution and on dilution with water the orange variety is obtained. The colourless variety also dissolves in caustic potash solution to a red solution but on acidification the original colourless variety is obtained. The orange variety dissolves in caustic potash and on acidification the colourless variety is obtained.

Action of Bromine and Reduction by Stannous Chloride.—Only acenaphthenequinone has, as in the case of the preceding azoxine, been identified from the reaction mixture after bromination or reduction with stannous chloride.

Action of Phenylhydrazine.—Orange needles (from a mixture of benzene and alcohol), m.p. 161°, were obtained by reacting the above phenazoxine with phenylhydrazine as in the previous case. (Found : N, 14·0 per cent.). The percentage of nitrogen is 50 per cent. above that is required by theory if the reaction goes in the way indicated by Kehrmann (*loc. cit.*).

Acenaphthylene-ψ-phenyloxazole and *N-benzylacenaphthylene-μ-phenyliminazole.*—An intimate mixture of acenaphthenequinone (2 g.) and freshly fused zinc chloride (1 g.) was added to benzylamine (4 g.) when a brisk effervescence set in. The mixture was then heated to 100° for some time and then at 190° until there was no evolution of ammonia. The reaction product which was obtained as a hard mass was treated with boiling alcohol and the oxazole was obtained from the alcoholic solution by precipitation with water. The precipitate was dissolved in the least quantity of benzene (charcoal) and petroleum ether added, when a greyish powder was obtained, m.p. 101°. Found : N, 4·6. $C_{19}H_{11}ON$ requires N, 5·2 per cent).

The iminazole was isolated from the alcohol-insoluble portion by crystallising from aniline in yellowish needles, m.p. 260°. It is almost insoluble in common organic solvents, but soluble in concentrated hydrochloric acid. (Found : N, 8·13. $C_{26}H_{18}N_2$ requires N, 7·86 per cent).

Acenaphthylene-oxazole and N-*Methylacenaphthylene-iminazole.*—Acenaphthenequinone (8 g.) and methylamine (33%, 100 c.c) were heated in a sealed tube for about 6 hours at 95-100°. As in the previous case the oxazole and iminazole were separated by treating the product with alcohol. The precipitate obtained by adding water to the alcoholic solution, was repeatedly dissolved in hydrochloric acid and precipitated by ammonia. Though very soluble in most of the organic solvents the oxazole could not be crystallised from any one of them and was obtained as a greyish amorphous powder, m p. 80-82°. (Found : N, 7·2. $C_{13}H_7ON$ requires N, 7·27 per cent).

The iminazole was obtained in minute yellowish needles not melting below 290° by dissolving the alcohol-insoluble portion in aniline and adding benzene drop by drop to the solution. It is insoluble in almost all common organic solvents. (Found : N, 13·12. $C_{14}H_{10}N_2$ requires N, 13·6 per cent).

Acenaphthylene-μ-methyloxazole and N-*Ethylacenaphthylene-μ-methyliminazole.*—Acenaphthenequinone (10 g.), ethylamine (10 c.c., 33%) and freshly fused zinc chloride (3 g.) were heated in a sealed tube for 8 hours at 160°. The oxazole and iminazole were separated by treating the black reaction product with alcohol. The solution in alcohol was poured into water and the precipitate dissolved in benzene (charcoal) and by adding light petroleum it was obtained as a microcrystalline powder, m. p. 115-17°. (Found : N, 6·65. $C_{14}H_9ON$ requires N, 6 76 per cent).

The portion insoluble in alcohol was washed with acetic acid and hot water. It was finally purified from benzene and obtained as a microcrystalline powder, m.p. above 290°. It is soluble in strong hydrochloric acid. (Found : N. 11·7. $C_{16}H_{14}N_2$ requires N, 11·96 per cent).

3-*Acetoxy-2-phenyl-4:5-acenaphthylene-furfurane.*— Acenaphthenequinone (10 g.), acetophenone (14 g.), acetic anhydride (65 g.) and sulphuric acid (*d* 1·84, 1·5 c.c.) were heated at 50° for 40 hours at 75-80°. The yellow product separating crystallised from benzene as light yellowish green needles, m.p. 257°. It is soluble in acetic acid, benzene and chloroform. (Found : C, 81·2; H, 4·06. $C_{22}H_{14}O_3$ requires C, 80·9 ; H, 4·2 per cent).

Action of Sodium Acetate and Acetic anhydride on Acenaphthenequinone.—Acenaphthenequinone (10 g.), freshly fused sodium acetate (10 g.) and acetic anhydride (60 g.) were heated for 4 hours on the water-bath until there was no quinone left. After keeping overnight the solidified mass was warmed and filtered off from the supernatant liquid. The brownish residue was washed with acetic acid in the cold and then repeatedly with water. The residue crystallised from glacial acetic acid as green nodules (A), not melting below 290°. It is sparingly soluble in acetic acid, insoluble in benzene, alcohol and ether. (Found : C, 80·54; H, 3·03 corresponding to the empirical formula $C_{13}H_6O_2$).

The deeply coloured acetic acid mother liquor was boiled with animal charcoal and diluted with water. The precipitate crystallised from dilute acetic acid in microscopic prisms (B) not melting below 290°. It is soluble in acetic acid and sparingly soluble in benzene and alcohol. (Found: C, 76·40 ; H, 3·6 corresponding to the empirical formula C_5H_3O).

The green product (A, 1 g.) was heated with a solution of caustic potash 10%, 25 c.c.) for 4 hours. On acidification an orange precipitate separated which when purified from alcohol was obtained as a microcrystalline powder, m.p. 240° (decomp.). (Found: C, 76·60; H, 3·8 corresponding to the empirical formula C_5H_3O).

The red substance (B, 1 g.) was boiled with a solution of caustic potash (10 %, 25 c.c.) and on acidification a yellow product separated which crystallised from alcohol in yellow needles, m.p. 230-31° (decomp.). It is found identical with the lactone of 8-hydroxy-acenaphthylglyoxylic acid (*vide infra*). (Found: C, 75·2; H, 3·1. $C_{14}H_6O_3$ requires C, 75·5; H, 2·7 per cent).

Action of Alcoholic Potash on Acenaphthenequinone.—A mixture of acenaphthenequinone (10 g.) and alcohol (50 c.c.) was heated with a solution of caustic potash (20 g. in 100 c.c. of alcohol) for 8 hours. The insoluble substance was separated, dissolved in hot water and the solution acidified with hydrochloric acid, when a yellow precipitate was obtained. This was filtered hot and on cooling a white precipitate was obtained, which crystallised from alcohol as colourless needles, m.p. 266°. It is identified to be naphthalic anhydride.

The yellow product (A) crystallised from alcohol as yellow needles, m.p. 230-31° (decomp.) and was identified to be the lactone of 8-hydroxyacenaphthyl-7-glyoxalic acid (*vide infra*). It is soluble in alcohol, benzene and chloroform. (Found: C, 75·78; H, 3·0. $C_{14}H_6O_3$ requires C, 75·5; H, 2·7 per cent).

The Condensation of Glycollic Acid with Acenaphthenequinone.—Finely powdered acenaphthenequinone (5 g.) and glycollic acid (25 g.) were mixed with methyl alcohol (300 c.c.) and then 40 g. of caustic potash added in small bits. It was now heated for 6 hours under reflux. Proceeding as in the case of the previous experiment a yellow crystalline substance, m.p. 230-31° (decomp.) was obtained. It dissolves in sulphuric acid with a blue fluorescence (brown solution).

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3. MAR. 19

Potentiometric Studies in Oxidation-Reduction Reactions. Part I. Oxidation with Potassium Iodate.

BY BALWANT SINGH AND IJAZ ILAHI.

Potassium iodate was first used by Andrews (*J. Amer. Chem. Soc.*, 1903, **25**, 756) for the titration of a number of reducing substances such as free iodine, iodides, arsenites and antimonites in presence of a large excess of concentrated hydrochloric acid. The method depends upon the formation of iodine monochloride and the disappearance of the iodine colour imparted to an immiscible solvent such as chloroform or carbon tetrachloride.

Lang (*Z. anorg. Chem.*, 1922, **122**, 332) has carried out fundamental investigations concerning direct titrations with potassium iodate in the presence of hydrogen cyanide. The end-point is again the disappearance of the iodine colour due to the formation of cyanide. The similarity of the two methods may be illustrated by the stoichiometric equations for the estimation of iodides.

$$HIO_3 + 2HI + 3HCl \rightarrow 3ICl + 8H_2O \quad \text{(Andrews)}$$

$$HIO_3 + 2HI + 3HCN \rightarrow 3ICN + 3H_2O \quad \text{(Lang)}$$

In all the reactions the iodate, in effecting oxidation, is reduced to iodide, which reacts with more iodate producing iodine, and this in turn reacts with more iodate to complete the reaction (Mitchel and Ward. "Modern Methods in Quantitative Chemical Analysis." 1932, p. 2).

Schoonover and Furman (*J. Amer. Chem. Soc.*, 1933, **55**, 3123) studied the oxidation of arsenious oxide with potassium iodate in hydrochloric and sulphuric acid solutions by a potentiometric method. They found that the concentration of the acid was an important factor in oxidation in hydrochloric acid. They proved that iodide, iodine or iodine monochloride were formed as the final reduction products of the iodate in the oxidation of arsenic depending upon the hydrogen-ion concentration. In a solution 4 to 6 normal in hydrochloric acid, iodine monochloride was formed as the final product.

The great stability of the potassium iodate solution and its non-interference with many kinds of organic matter make these methods applicable to cases in which the potassium permanganate method could not be used satisfactorily.

Jamieson ("Volumetric Iodate Methods", 1926) has made a thorough investigation into the applicability of Andrew's method. He has shown that it is advantageous in a few cases, particularly where very small quantities of a substance are to be determined, to add a small quantity of iodine monochloride dissolved in hydrochloric acid and to titrate the liberated iodine against potassium iodate solution.

In the present investigation thallous, stannous, mercurous, antimonious, and arsenious salts have been determined potentiometrically by titrating against standard potassium iodate in presence of concentrated hydrochloric acid.

EXPERIMENTAL.

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in the solution to be titrated, was coupled with a saturated calomel electrode through an agar-agar-KCl bridge. The cell was placed in a water-bath, the temperature of which was maintained at 10°. The E. M. F. of the cell was read on a potentiometer scale (Potentiometer, Cambridge Instrument Co. Ltd., England).

A standard solution of potassium iodate was prepared by dissolving the calculated quantity of the pure dry analytical reagent in the water. The solution required no further standardisation and was permanent. According to Jamieson (*loc. cit.*) a solution of potassium iodate was kept for 10 years without a change of strength.

A known weight of each salt was weighed into a titration vessel and the required amount of concentrated hydrochloric acid added to keep its concentration above 4*N*. Standard potassium iodate was added from a burette, the mixture stirred by a mechanical stirrer and the progress of the oxidation followed with the potentiometer.

A series of potentiometric titrations were performed with different amounts of each salt. One titration for every salt, as typical of that set, is recorded in the following tables.

TABLE I.

Titration of thallous chloride (0·1193 g.) mixed with 20 c.c. of water and 25 c.c. of conc. HCl, against KIO_3 ($M/20$).

KIO_3.	E. M. F. (volts).	$\Delta E/\Delta C$ (m. volt/c.c.).
3·50 c.c.	0·520	
		60
4·00	0·550	
		90
4·40	0·586	
		85
4·60	0·603	
		100
4·80	0·623	
		193
4·95	0·652	
		4660
5·00	0·885	
		500
5·05	0·910	
		300
5·10	0·925	
		125
5·30	0·950	
		40
5·80	0·970	
		5
6·80	0·975	

TABLE II.

Titration of stannous chloride (0·1127 g.) mixed with 20 c.c. of water and 25 c.c. of conc. HCl, against KIO_3 ($M/20$).

KIO_3.	E. M. F. (volts).	$\Delta E/\Delta C$ (m. volt/c.c.).
4·00 c.c.	0·528	
		105
4·20	0·549	
		80
4·40	0·565	
		100
4·60	0·585	
		105
4·80	0·606	
		120
4·90	0·618	
		380
4·95	0·637	
		4060
5·00	0·840	
		300
5·10	0·870	
		110
5·30	0·892	
		36
5·80	0·910	
		8
6·80	0·918	

TABLE III.

Titration of mercurous chloride (0·2354 g.) mixed with 20 c.c. of water and 25 c.c. of conc. HCl, against KIO_3 ($M/20$).

KIO_3.	E. M. F. (volt).	$\Delta E/\Delta C$ (m. volt/c.c.).
3·00 c.c.	0·504	
		37
4·00	0·541	
		54
4·50	0·568	
		85
4·70	0·585	
		90
4·80	0·594	
		507
4·95	0·670	
		4000
5·00	0·870	
		480
5·05	0·894	
		320
5·10	0·910	
		200
5·20	0·930	
		33
5·50	0·940	
		33
5·80	0·950	
		6
6·80	0·956	

TABLE IV.

Titration of potassium antimonyl tartrate (0·3240 g.) mixed with 20 c.c. of water and 25 c.c. of conc. HCl, against KIO_3 ($M/20$).

KIO_3.	E. M. F. (volt).	$\Delta E/\Delta C$ (m. volt/c.c.).
9·00 c.c.	0·630	
		30
9·20	0·636	
		30
9·40	0·642	
		25
9·60	0·647	
		45
9·80	0·656	
		70
9·90	0·663	
		120
9·95	0·669	
		3520
10·00	0·845	
		100
10·05	0·850	
		100
10·15	0·860	
		80
10·40	0·880	
		38
10·80	0·895	
		13
11·80	0·908	

TABLE V.

Titration of arsenious oxide (0·0989 g.) mixed with 20 c.c. of water and 25 c.c. of conc. HCl, against KIO_3 ($M/20$).

KIO_3.	E. M. F. (volt).	$\Delta E/\Delta C$ (m. volt/c.c.).
8·00 c.c.	0·482	
		54
9·00	0·536	
		63
9·40	0·561	
		75
9·60	0·576	
		70
9·80	0·590	
		140
9·90	0·604	
		480
9·95	0·628	
		4240
10·00	0·840	
		500
10·05	0·865	
		230
10·15	0·888	
		45
10·35	0·897	
		36
10·85	0·915	
		14
11·90	0·930	

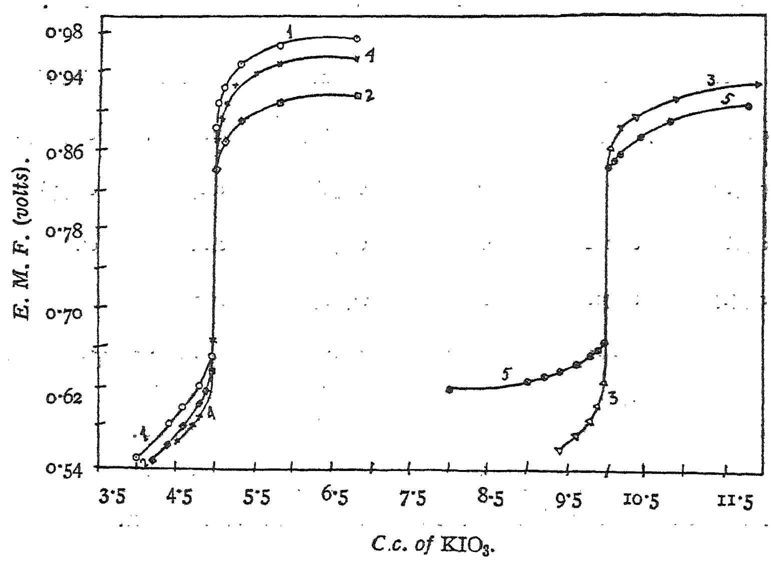
The curves for the above titration are given in Fig. 1.

DISCUSSION.

In these titrations, with the addition of standard potassium iodate the E. M. F. rose steadily till the equivalence point. At the equivalence-point, there was a sharp jump in potential in each case. For the addition of 0·05 c.c. of the titrant, the inflection potential was of the order of 233, 203, 200, 176 and 212 millivolts for thallous chloride, stannous chloride, mercurous chloride, potassium antimonyl tartrate and arsenious oxide respectively. After the equivalence-point, there was again a rise in the potential which became steady on further addition of the reagent.

FIG 1.

Potassium iodate titration.



Curves 1—5 refer respectively to thallous chloride, stannous chloride, sodium arsenite, mercurous chloride and pot. antim. tartrate.

From the volume of the potassium iodate solution required in each titration corresponding to the equivalence-point, the amount of the salt was calculated. The values obtained are compared with the amounts of the salt taken in Table VI.

TABLE VI.

Thallous chloride		Stannous chloride	
Taken.	Found.	Taken.	Found.
0·1193 g.	0·1194 g.	0·1127	0·1124
0·2396	0·2394	0·2250	0·2252
0·3588	0·3586	0·3385	0·3383
0·4763	0·4762	0·4513	0·4514

TABLE VI (contd.).

Mercurous chloride.		Pot. antim. tartrate.		Arsenious oxide.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0·2354 g.	0·2351 g.	0·3240 g.	0·3242 g.	0·0989 g.	0·0987 g.
0·4720	0·4718	0·4517	0·4518	0·1979	0.1978
0·7082	0·7081	0·6789	0·6788	0·2866	0·2866
0·9413	0·9412	0·7886	0·7884	0·4598	0·4596

These results show that thallous chloride, stannous chloride, mercurous chloride, potassium antimonyl tartrate and arsenious oxide can be determined quantitatively by the potentiometric method.

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Properties of Activated Sugar Charcoal Coated with Various Substances. Part I. Liberation of Acid and Alkali by the Action of Neutral Salts in Relation to the Surface Charge.

By Harendra Kumar Acharya.

Surfaces of charcoal activated at moderate temperatures up to about 500° appears to contain acidic substances (Kolthoff, *J. Amer. Chem. Soc.*, 1932, **54**, 4473). The formation of different types of oxides on the surface has been assumed at different temperatures (Schilov and co-workers, *Z. physikal. Chem.*, 1930, **148**, 233; *ibid.*, 1930, **149**, 211). It has also been suggested (Ockrent, *J. Chem. Soc.*, 1934, **291**) that the properties of activated charcoal are mainly the result of an activated layer of water molecules on the surface. A relationship appears to exist between the primarily adsorbed ions on the surface and its charge, the liberation of acid or alkali by neutral salts of strong acids and bases, and the adsorption of strong acids and strong bases (Roychoudhury, *J. Indian Chem. Soc.*, 1931, **8**, 433; Roychoudhury and Mukherjee, *Kolloid Z.*, 1931, **57**, 302; *Z. physikal. Chem.*, 1931, **157**, 435). In the light of these considerations experiments were undertaken to treat activated sugar charcoal with different substances so as to produce surface coats, or, primarily adsorbed layers of known nature and to study their properties with respect to the factors just mentioned. It will be seen below that coats produced by organic acids give surfaces which have a negative charge and simultaneously contain hydrogen ions replaceable with ease by neutral alkali or alkaline earth salts. Treatment with amines on the other hand favours the formation of surfaces having weaker negative charge and easily replaceable hydroxyl ions or showing a decrease in the amount of replaceable hydrogen ions. Several amino-acids, mercaptan, ketones and an aldehyde have also been used.

EXPERIMENTAL.

The sugar charcoal X (for preparation see the paper to be communicated by Acharya and Ray to *J. Indian Chem. Soc.*) used as a basis for the coats was obtained by the activation of pure sugar charcoal at 600° for 6 hours in air at 1 mm. of Hg. It had a weak negative charge in contact with water. The electro-osmotic rates were determined in the manner used by Roychoudhury (*loc. cit.*).

The sample Y (*vide* Table XIV) was iso-electric with water (null charcoal) and was obtained by further activating X at 600° for another 4 hours under the same pressure of air. On treatment with a neutral electrolyte, Y liberated slight traces of alkali, while X liberated small quantities of acid.

2 G. of the activated charcoal X were kept in contact for 24 hours with 10 c.c. alcoholic solutions containing 0·02 g. of the organic substance. The alcohol was then evaporated and the charcoal dried in a silica crucible on a water-bath. The charcoal thus treated was further activated in some cases. The various resulting charcoals were divided into two parts, A and B.

'A' was again divided into about two equal parts, A_1 and A_2 in two cleansed, steamed and dried Jena glass bottles. 40 C.c. of conductivity water and 40 c.c. of the electrolyte solution were added respectively to A_1 and A_2. The mixtures were shaken and kept in contact for 24 hours. The upper liquid was seperated by means of a powerful centrifuge and the p_H values of the supernatant liquid were determined (*a*) by indicators using Hellige's immersion colorimeter, and (*b*) also by the quinhydrone electrode. The p_H values measured by these methods are given respectively under M_1 and M_2 in the table. The following indicators have been used (*cf.* Clark, "Determination of Hydrogen Ions", 1928, pp. 93-94).

I. Bromophenol blue p_H range 3·0-4·6; p_K 3·98. II. Methyl red, 4·2-6·3; p_K 5·0. III. Bromocresol purple, 5·2-6·8; p_K 6·3. IV. Bromothymol blue 6·0-7·6, p_K 7·0. The salt effect of the indicators are I. $(-0·28) - (-0·35)$, II. $(-0·04) - (+0·10)$, III. $(-0·25) - (-0·26)$ and IV. $(-0·17) - (-0·19)$ according to different authors for the concentrations of salt used (Clark, *loc. cit.*, p. 181).

Indicator readings have been compared in a number of cases with those with the quinhydrone electrode, the difference in the two sets of values seems to be negligible. Where two indicators could be used for the same p_H determination, the difference is small (*e.g.*, p_H of an HCl solution by I, 4·43 and by II, 4·55) but the difference between values obtained with III and IV is apreciable for poorly buffered or unbuffered solutions (*e.g.*, p_H of a sample of conductivity water by III, 5·64 and by IV, 6·42).

'B' was washed repeatedly with conductivity water till the p_H of the supernatant liquid was about 6. The charcoal was then dried in a silica crucible on a water-bath and divided into two equal parts B_1 and B_2 which were treated respectively as A_1 and A_2.

The p_H of the conductivity water (6·42 with indicator IV), the pure electrolyte solutions and the same electrolyte solution kept in contact with the startingsamples X and Y were also determined* under identical conditions.

Normal concentrations of the electrolytes were employed unless otherwise stated.

RESULTS AND DISCUSSIONS.

TABLE I.

Charge measurements.

	Treatment of charcoal.	Rate of electro-osmosis. (Movement of the air bubble in three minutes.)
1.	X in contact with water	−2·5 cm.
1(*a*).	X_1, obtained by coating X with palmitic acid, in contact with water	−12·7cm.
1(*b*).	X_1 and N/10,000 KCl solution	−0·4 cm.
2.	Z, prepared as X but activated in air at a pressure of 4 mm. of Hg. in contact with water.	−3·8 cm.
2(*a*).	Z_1 obtained by coating Z with palmitic acid, in contact with water.	−13·0 cm.
2(*b*).	Z_1 and *N*/10,000 solutions of the following electrolytes.	
	I. KCl	−0·8 cm.
	II. NaCl	−1.9 cm.
	III. LiCl	−4·3 cm.
	IV. $BaCl_2$	−9·2 cm.

It will be seen that on being coated with an insoluble organic acid the negative charge of the charcoal surface increases, which again diminishes on being treated with neutral salt solutions and that the capacity of the cations to diminish the surface charge of the charcoal lies in the order K > Na > Li > Ba.

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* With indicator IV the following values were obtained; *N*-KCl, p_H = 6·28, *N*-KCl in contact with charcoal for sample X, p_H = 6·22, for sample Y, p_H = 6·32.

According to Mukherjee (*Trans. Faraday Soc.*, 1921, **16**, 103; *Phil. Mag.*, 1922, *vi*, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 219; *Kolloid Z.*, 1929, **49**, 362) this negative charge shows that a primarily adsorbed anion layer is present on the surfaces and H°-ions are most likely to be held in the neighbourhood of the surface of the charcoal by electrostatic attraction. Such of these H°-ions as are present on the liquid side of the double layer are mobile and are easily replaceable by cations from neutral salt solutions. The different cations should have the power of liberating H°-ions indicated by their capacity to diminish the negative charge on the surface. This expectation is confirmed by the following observations with charcoal coated with palmitic, stearic, lauric and myristic acids which have similar properties.

TABLE II.

Palmitic acid coat.

Electrolyte.	C_1*		A_1.	A_2.		Difference in p_H unit.
	M_1.	M_2.	M_1.	M_1.	M_2.	(C_1-A_2).
KCl	6·28	6·25	5·19	4·01	4·01	2·27 (acid)
NaCl	6·39		,,	4.28		2·11
LiCl	6·70		,,	4·85	4·83	1·85
RbCl	5·75		,,	4·20		1·55
$SrCl_2$	6·23		,,	5·28		0·95
$BaCl_2$	6·25		,,	5·58		0·67

TABLE III.

Stearic acid coat.

Electrolyte.	C_1.	A_1.	A_2.		Difference in p_H unit.
	M_1.	M_1.	M_1.	M_2.	$(C_1-A_2.)$
KCl	6·28	5·09	4·19		2·09 (acid)
NaCl	6.39	,,	4·50	4·50	1·89
LiCl	6·70	,,	5·05		1·65
RbCl	5·75	,,	4·31		1·44
$SrCl_2$	6·23	,,	5·85		0·38
$BaCl_2$	6·25	,,	6·00		0·25

* C_1 indicates the p_H values of the pure electrolyte solution.

TABLE IV.

Lauric acid coat.

Electrolyte.	C_1.	A_1.	A_2.		Difference in p_H unit..
	M_1.	M_1.	M_1.	M_2.	(C_1-A_2).
KCl	6·28	5·28	4·20	4·18	2·08 (acid)
NaCl	6·39	,,	4·55		1·84
LiCl	6·70	,,	5·05		1·65
RbCl	5·75	,,	4·37		1·38
$SrCl_2$	6·23	,,	5·39		0·84
$BaCl_2$	6·25	,,	5·45		0·80

TABLE V.

Myristic acid coat.

Electrolyte.	C_1.	A_1.	A_2.		Difference in p_H unit.
	M_1.	M_1.	M_1.	M_2.	(C_1-A_2).
KCl	6·28	5·47	4·22	4·20	2·06 (acid)
NaCl	6·39	,,	4·47		1·92
LiCl	6·70	,,	5·26		1·44
RbCl	5·75	,,	4·37		1·38
$SrCl_2$	6·23	,,	5·39		0·84
$BaCl_2$	6·25	,,	5·70	5·65	0·45

The difference in p_H diminishes in the order K > Na > Li > Rb > Sr > Ba in agreement with the order K > Na > Li > Ba for the effect of these ions on the electric charge.

The order is, however, different from the order of valency and mobility deduced by Mukherjee (*loc. cit.*) from theoretical considerations, which holds good for a large number of systems.

Recently Wiegner (*Trans. Third Inter. Cong. Soil Sci.*, 1935, **3**, 5) has shown from extensive measurements that the departure from the theoretical series in the cases investigated by him and his co-workers arises out of the ultraporous structure (*cf.* Herbst, *Biochem. Z.*, 1921, **115**, 204; Dubinin, *Z. physikal. Chem.*, 1930, **150**, 145; Bell and Philip, *J. Chem. Soc.*, 1934, 1164) and the consequent differences in the accessibility of different parts of the surface which is determined by the size of the ions. He finds (*loc. cit.*) that the larger the radius of the ion, the less is the amount of cation exchanged. In addition the intensity of the adsorption which depends on the free energy of the formation of the ion pair formed by the primarily and electrically adsorbed ions (Mukherjee, *loc. cit.*) requires to be considered. The surface may also have both cations and anions in the primarily adsorbed layer. It appears, however, that the mobility and the size of the hydrated cation are the main factors responsible for the observed series. According to Hevesey (*Kolloid Z.*, 1917, **21**, 130) electrolytic ions are surrounded by an envelope of water of a thickness such that they attain more or less the same potential on their periphery. Divalent ions are, therefore, liable to have a larger diameter than univalent ions. For ions with the same valency the mobility would vary inversely as the size of the ions. If these premises be true, the series Rb > K > Na > Li > Ba > Sr would result. The position of rubidium and strontium does not agree with this series.

In view of the greatest effect of KCl, this electrolyte has been used in the succeeding investigations on the comparative effects of coatings with different organic acids.

TABLE VI.

Coat of	A_1.		A_2.		Difference in p_H unit.
	M_1.	M_2.	M_1.	M_2.	
Lauric acid	5·28	5·28	4·01	3·99	1·27 (acid)
Myristic ,,	5·47		4·15		1·32 ,,
Palmitic ,,	5·19	5·19	4·01	3·99	1·18 ,,
Stearic ,,	5·09		3·92		1·17 ,,
Hippuric ,,	4·70		3·77		0·93 ,,
Oleic ,,	5·53	5·53	3·67	3·67	1·86 ,,
Amino-salicylic ,,	4·15		3·60		0·55 ,,
Amino-benzoic ,,	4·33		3·50		0·83 ,,
Cinnamic ,,	4·43		3·73		0·70 ,,

The different acids appear to produce coatings with easily replaceable hydrogen ions of comparable amounts. The p_H of the water in contact with charcoal (A_1 values) show wide variations. The samples were, therefore, washed and the B values (*vide* experimental section) were obtained.

TABLE VII.

Sample X.

Coat of	B_1.		B_2.		Difference in p_H unit.
	M_1.	M_2.	M_1.	M_2.	
Lauric acid	6·15	6·14	4·26	4·21	1·89 (acid)
Myristic ,,	6·20		4·10		2·10 ,,
Palmitic ,,	6·00	6·10	3·87	3·87	2·13 ,,
Stearic ,,	6·20		4·10		2·10 ,,
Hippuric ,,	6·10		3·87		2·23 ,,
Oleic ,,	6·15	6·15	3·57	3·58	2·58 ,,
Amino-salicylic ,,	6·15		4·01		2·14 ,,
Amino-benzoic ,,	6·00		3·96		2·04 ,,
Cinnamic ,,	6·10		3·92		2·18 ,,

The difference in p_H is increased. It seems that most of the free acid has been washed off and the washing may also be expected to diminish the thickness of the coat. Results of activation, at 250° for 2 hours of the charcoal X, coated with the acids have been given in Tables VIII and IX. The decrease of the p_H persists even after such activation.

TABLE VIII.

Coat of	A_1.		A_2.		Difference in p_H unit.
	M_1.	M_2.	M_1.	M_2.	
Lauric acid	5·85		4·80		1·05 (acid)
Myristic ,,	6·15		5·41		0·74 ,,
Palmitic ,,	5·85	5·83	4·58		1·27 ,,
Stearic ,,	6·00		5·02		0·98 ,,

TABLE IX.

Coat of	B₁. M₁.	B₁. M₂.	B₂. M₁.	B₂. M₂.	Difference in p_H unit.
Lauric acid	6·20	6·18	5·19	5·19	1·01 (acid)
Myristic ,,	6·25		5·37		0·88 ,,
Palmitic ,,	6·20		4·33		1·47 ,,
Stearic ,,	6·15		5·09		1·06 ,,

The coats as prepared by the evaporation on a water-bath may consist of a layer of the organic acid, several molecules thick at places. The activation at 250° ensures that we are dealing with thinner layers or layers present in patches, *i.e.*, which do not cover the whole surface. The extent of the decrease of p_H on the addition of a solution of potassium chloride diminishes on activating the charcoal previously coated with the above acids at 250° for 2 hours and finally the solution turns slightly alkaline on activation at 600° for the same duration (*vide* Table X).

TABLE X.

Coat of	A₁. M₁.	A₂. M₁.	Difference in p_H unit.
Lauric acid	6·40	6·69	0·29 (alkali)
Myristic ,,	6·46	6·67	0·21 ,,
Palmitic ,,	6·39	6·69	0·30 ,,
Stearic ,,	6·45	6·90	0·45 ,,

This observation shows that the acidic substances on charcoal surface are gradually decomposed on being activated at a lower temperature, while at a higher temperature they are destroyed as a result of which the charge of the charcoal surface decreases to zero as observed by Roychoudhury (*loc. cit.*). Such a charcoal liberates alkali with neutral salt solution (Roychoudhury and Mukherjee, *loc. cit.*).

Coats of substances other than organic acids.

TABLE XI.

Coat of	A_1.		A_2.		Difference in p_H unit.
	M_1.	M_2.	M_1.	M_2.	
Benzyl mercaptan	6·27	6·29	4·29	4·30	1·98 (acid)
Formaldehyde	5·73		4·70		1·03 ,,
Acetone	6·00		4·01		1·99 ,,
Vaniline	5·12		3·96		1·16 ,,

The p_H also decreases with coatings of these substances.

It is well known that charcoal holds oxygen very tenaciously. As early as 1867, Calvert (*J. Chem. Soc.*, 1867, **29**, 293) using comparatively pure charcoal showed the extraordinary activity of the adsorbed oxygen, which took part with ease in many reactions, *e.g.*, the oxidation of ethyl alcohol to acetic acid, while the free gas could not effect it. Later Reed and Wheeler (*J. Chem. Soc.*, 1912, **101**, 831), Schilov and co-workers (*loc. cit.*, *Z. physikal. Chem.*, 1930, **150**, 31) and others emphasised the part played by oxygen in the adsorption by charcoal.

It seems that the aldehydes and ketones are oxidised on the charcoal surface to their corresponding acids, by the highly active oxygen, adsorbed on the charcoal and that such of the hydrogen ions of the acids, thus formed, which are present in the mobile sheet of the double layer are easily replaced by cations.

TABLE XII.

Charge measurements.

	Treatment of charcoal.	Rate of electro-osmosis (movement of the air bubble in 3 min.).
1.	P (activated at 900° for 6 hrs. in air at a pressure of 3 mm. of Hg) in contact with water	0
1(a).	P_1 (obtained by coating P with α-naphthylamine) in contact with water	0
1(b).	P_1 and $N/10{,}000$-KCl solution	−2 cm.
2.	Q (activated at 600° for 6 hrs. in air at a pressure of 3 mm. Hg) in contact with water	−3·6 cm.
2(a).	Q_1 (obtained by coating Q with α-naphthylamine) in contact with water	−2 cm.
2(b).	Q_1 and $N/10{,}000$-KCl solution	−5·0 cm.

TABLE XII (contd.).

Charge measurements

Treatment of charcoal.	Rate of electro-osmosis (movement of the air bubble in 3 min).
3. R (purified by washing but unactivated) in contact with water	– 9·0 cm.
3(a). R_1 (obtained by coating R with α-naphthylamine) in contact with water	—6·0 cm.
3(b). R_1 and *N*/10,000-KCl solution	—1·6 cm.

It appears that on treatment with amine the nature of the surface changes. It developes a capacity to assume a negative charge in contact with the electrolyte presumably by an adsorption of the anion as the electrolyte no longer diminishes the negative charge but increases it. Positive sugar charcoal which has been activated at 900° has a tendency to adsorb chlorine ions (*vide* Roychoudhury, *loc. cit.*). With negatively charged surfaces, the electrical adsorption of the K° ions preponderates. Perhaps the adsorption of chlorine ion is more general and of the nature of a primary adsorption and is further facilitated by the amine ions present on the surface.

TABLE XIII.

Coats of	Amout of amine per g. of charcoal.	A_1. M_1.	A_2. M_1.	Difference in p_H unit.
Diphenylamine	0·01	6·42 ; 6·42	6·21 ; 6·21	0·21 (acid)
	0·1	6·53	6·75	0.22 (alkali)
	0·2	6·62 ; 6·65	7·01 ; 7·03	0·38 ,,
α-Naphthylamine	0·01	6·46	6·39	0·07 (acid)
	0·1	6·57	6·99	0·42 (alkali)
	0·2	6·66 ; 6·66	7·12 ; 7·19	0·46 ,,
Toluenediamine	0·01	6·42	6·56	0·14 ,,
	0·1	6·58	6·90	0·32 ,,
		—	—	
Phenylenediamine	0·01	6·40	6·51	0·11 ,,
	0·1	6·52	6·82	0·30 ,,

TABLE XIV.

Iso-electric charcoal.

Sample Y.

Coat of	Conc. of KCl	A_1. M_1	A_2. M_1	Difference in p_H unit.
Diphenylamine	0·025 *N*	6·44 ; 6·44	6·63 ; 6·67	0·19 (alkali)
	1·0	,,	6·67	0.23 ,,
	2·0	,,	6·69	0·25 ,,
α-Naphthylamine	0·025 *N*	6·40 ; 6·41	6·65	0·15 ,,
	1·0	,,	6·80	0·40 ,,
	2·0	6·0 ; 6·41	6·93 ; 7·01	0·53 ,,
Toluenediamine	0·025 *N*	6·57	6·70	0.13 ,,
	1·0	,,	6·93	0·36 ,,
	2·0	,,	7·16	0·59 ,,

It will be seen from Tables XIII and XIV that the amount of alkali, liberated by potassium chloride solution from the charcoal surface coated with amines, depends on three factors, such as the charge of the charcoal, amount of the amine per g. of charcoal and the concentration of the potassium chloride solution added.

The results obtained in Tables XIII and XIV are easily understood from our observations and from those of Kruyt and Kadt (*Kolloid Beihefte*, 1931, **32**, 249) who have shown that oxygen-free charcoal carries a positive charge which should according to Mukherjee (*loc. cit.*) liberate alkali. The charcoal used in Table XIII, contains some acidic substances on its surface but on treating with increasing amounts of the amines, the proportion of the amine-covered area increases. The surface has possibly a composite character and the acid liberating patches gradually diminish in proportion as the alkali liberating patches increase. Table XIV shows that liberation of the alkali increases with the increase in the concentration of the electrolyte. Since charcoal activated at high temperatures and without an amine coating can liberate alkali, it is not possible to attribute this property solely to the amine. At the same time treatment with the amine appears to favour an increase in the proportion of such patches or alternatively the diminution of the acid patches. The positive charge observed in several cases as the result of activation at high temperatures seem to suggest that the charcoal surface has a primarily absorbed layer of cations. Adsorption of hydrogen ions by the weakly basic adsorbed amine groups may be responsible for the formation of the primarily adsorbed cation layer which gives a positive charge to the surface and leads to a liberation of the electrically adsorbed or mobile hydroxyl ions on addition of neutral salts.

SUMMARY.

1. Coats of different insoluble organic substances have been formed from their alcoholic solutions on activated sugar charcoal and their properties have been studied with respect to their surface charge and the liberation of acid or alkali by neutral salt solutions.

2. The acid coats increase the surface negative charge, which diminishes on being treated with neutral salt solutions in the order $KCl > NaCl > LiCl > BaCl_2$.

3. Acid is liberated from the acid coats by neutral salt solutions in the order corresponding with their capacity to diminish the surface negative charge, $KCl > NaCl > LiCl > RbCl > SrCl_2 > BaCl_2$.

4. Activation of the coated charcoal diminishes the amount of acid liberated.

5. Similar acid liberating coats can also be obtained with mercaptan, aldehyde and ketones.

6. Amine coats diminishes the surface negatitve charge, which increases on being treated with neutral salt solutions. Alkali is liberated from amine coats by neutral salt solution and the amount depends on the initial charge of the charcoal, the concentration of the neutral salt solution and the amount of amine per g. of charcoal.

My best thanks are due to Prof. J. N. Mukherjee for suggesting this work and for facilities.

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Dihydroresorcinols. Part IV. The Condensation of Phenyldihydroresorcinol with Aromatic Aldehydes.

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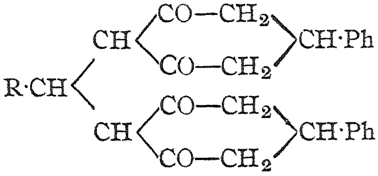
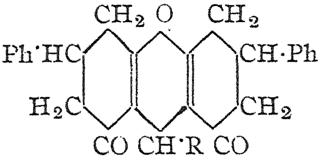
In extending our work on the condensation of aldehydes with dihydroresorcinols, we have condensed phenyldihydroresorcinol with salicylaldehyde, benzaldehyde, cinnamic aldehyde, furfuraldehyde, piperonal, vanillin, *o*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. The bis-derivative (I) was formed in each case in presence of piperidine, at the ordinary temperature, and this could be dehydrated to the octahydroxanthene derivative by the methods reported in earlier papers (*J. Indian Chem. Soc.*, 1933, **10**, 663; *J. Univ. Bombay*, 1933, **2**, *ii*, 62).

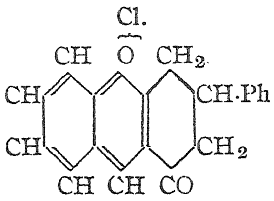


(I)

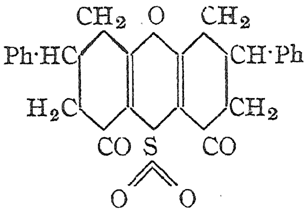


(II)

In presence of gaseous hydrogen chloride, however, phenyldihydroresorcinol reacted with salicylaldehyde giving 2-phenyl-4-keto-1:2:3:4-tetrahydrobenzopyranol anhydrochloride (III). Chloral hydrate and thionyl chloride also underwent condensation readily, and the former gave 1-phenyl-4(α-hydroxy-βββ-trichloroethyl)-*cyclo*hexane-3:5-dione (IV). We have provisionally assumed the structure of the oxide of 2:7-diphenyl-4:5-diketo-1:2:3:4:5:6:7:8-octahydrophenothioxin (V) for the product obtained from thionyl chloride. Dimethyldihydroresorcinol condensed similarly with these reagents and we are studying their degradation to the known phenothioxin derivatives (Shri Krishna, *J. Chem. Soc.*, 1923, **123**, 2782; Mauthner *Ber.*, 1905, **38**, 1411; Hildich and Smiles, *J. Chem. Soc.*, 1911, **99**, 408).



(III)



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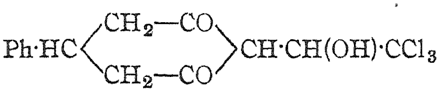

$$Ph{\cdot}HC\left\langle\begin{matrix}CH_2{-}CO\\CH_2{-}CO\end{matrix}\right\rangle CH{\cdot}CH(OH){\cdot}CCl_3$$

(IV)

Finally we have studied the condensation of furfural and *p*-dimethylaminobenzaldehyde with dimethyldihyroresorcinol, as these products were required for comparison with their analogues from phenyldihydroresorcinol. Our conclusion is that so far as the condensation of aldehydes is concerned, all the dihydroresorcinols behave similarly, the substituents in position-4 having no effect on the reactivity of the methylene group.

EXPERIMENTAL.

Phenyldihydroresorcinol was prepared by the method of Vorländer (*Annalen*, 1897, **294**, 253). The hydrolysis of the dione ester was carried out by alcoholic potash, as this required only 3-4 hours, yield 80-85%.

Salical-bisphenyldihydroresorcinol.—A mixture of salicylaldehyde (1 g.), phenyldihydroresorcinol (3 g.), dry methyl alcohol (15 c.c.) and piperidine (4 drops) was kept at the ordinary temperature for 12 hours. The alcohol was removed by suction and the residue crystallised from dilute ethyl alcohol in short orange needles, m.p. 169-70°. The alcoholic solution gave brown colouration with ferric chloride. (Found: C, 77·3; H, 5·9. $C_{31}H_{28}O_5$ requires C, 77·5; H, 5·8 per cent).

When its solution in absolute ethyl alcohol was saturated with hydrogen chloride and kept for 24 hours, *2:7-diphenyl-4:5-diketo-9-o-hydroxyphenyl-octahydroxanthene* was obtained, which crystallised from alcohol in short yellow needles, m.p. 230°. (Found: C, 80·2; H, 5·8. $C_{31}H_{26}O_4$ requires C, 80·5; H, 5·6 per cent).

The *acetyl* derivative, prepared by heating the bis-compound with acetic anhydride for 6 hours, crystallised from dilute alcohol in crimson-red short needles, m.p. 145°. (Found: C, 78·4; H, 5·6. $C_{33}H_{28}O_5$ requires C, 78·6; H, 5·5 per cent).

2-Phenyl-4-keto-1:2:3:4-tetrahydrobenzopyranol anhydrochloride.— A solution of salicylaldehyde (2 g.), phenyldihydroresorcinol (3 g.) in dry methyl alcohol (15 c.c.) was saturated with hydrogen chloride at 0°. The mixture became warm, changed to red and after some time began depositing red crystals, which were removed after 12 hours, washed with methyl alcohol and dried in vacuum over caustic potash. The substance contained chlorine and showed no tendency to melt up to 360°, but simply carbonised. (Found: C, 73·1; H, 4·9. $C_{19}H_{15}O_2Cl$ requires C, 73·4; H, 4·8 per cent).

The *anhydro-base*, prepared by adding sodium acetate solution to the warm solution of the anhydrochloride in a large excess of ethyl alcohol, was a pinkish powder, insoluble in most of the organic solvents, and did not melt below 360°. It was stable to concentrated alcoholic potash solution, and regenerated the anhydrochloride on treating with methyl alcoholic hydrogen chloride. (Found: C, 77·8; H, 5·6. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5 per cent).

Benzal-bis-phenyldihydroresorcinol, prepared from benzaldehyde, crystallised from dilute alcohol in white needles, m.p. 110°. (Found : C, 80·1; H, 6·1. Calc. for $C_{31}H_{28}O_4$: C, 80·1; H, 6·0 per cent).

The *xanthene* derivative crystallised from alcohol in colourless needles, m.p. 228°. (Found : C, 83·0; H, 6·0. Calc. for $C_{31}H_{26}O_3$: C, 83·4; H, 5·8 per cent). (Vorländer, *Annalen*, 1899, **309**, 379).

Cinnamal-bisphenyldihydroresorcinol crystallised from alcohol in short yellow needles, m.p. 155-56°. (Found : C, 80·4; H, 6·3. $C_{33}H_{30}O_4$ requires C, 80·8; H, 6·1 per cent).

The *xanthene* derivative crystallised from alcohol in yellow needles, not melting below 280°. (Found : C, 83·4; H, 6·1. $C_{33}H_{28}O_3$ requires C, 83·9; H, 5·9 per cent).

Furfuralbisphenyldihydroresorcinol crystallised from alcohol in white needles, m.p. 122°. (Found : C, 76·6; H, 5·7. $C_{29}H_{26}O_5$ requires C, 76·4; H, 5·8 per cent).

The *xanthene* derivative crystallised from alcohol as a black microcrystalline powder, m.p. above 280°. (Found : C, 80·1; H, 5·5. $C_{29}H_{24}O_4$ requires C, 79·8; H, 5·5 per cent).

p-*Dimethylaminobenzal-bisphenyldihydroresorcinol*, prepared from *p*-dimethylaminobenzaldehyde, crystallised from alcohol in orange needles, m.p. 107°-108°. (Found: C, 78·2; H, 6·4. $C_{33}H_{33}O_4N$ requires C, 78·1; H, 6·5 per cent).

The *xanthene* derivative crystallised from alcohol in small yellow needles, m.p. 200°. (Found : C, 80·9; H, 6·3. $C_{33}H_{31}O_3N$ requires C, 80·8; H, 6·2 per cent).

3 : 4-*Methylenedioxybenzal-bisphenyldihydroresorcinol*, prepared from piperonal, crystallised from alcohol in colourless, prismatic needles, m.p. 148°. (Found : C, 75·31; H, 5·8. $C_{32}H_{28}O_6$ requires C, 75·6; H, 5·5 per cent).

The *xanthene* crystallised from alcohol in colourless needles, m.p. above 280°. (Found : C, 78·0: H, 5·6. $C_{32}H_{26}O_5$ requires C, 78·3; H, 5·3 per cent).

4-*Hydroxy*-3-*methoxybenzal-bisphenyldihydroresorcinol*, prepared from vanillin, crystallised from alcohol in pale yellow needles, m.p. 116°. (Found : C, 75·1; H, 5·8. $C_{32}H_{30}O_6$ requires C, 75·2; H, 5·8 per cent).

The *xanthene* derivative crystallised from alcohol in white needles, m.p. above 280°. (Found : C, 77·8; H, 5·9. $C_{32}H_{28}O_5$ requires C, 78·0; H, 5·6 per cent).

o-*Nitrobenzalbisphenyldihydroresorcinol* crystallised from alcohol, in pale yellow needles, m.p. 160°. (Found : C, 73·0; H, 5·4. $C_{31}H_{27}O_6N$ requires C, 73·1; H, 5·3 per cent).

The *xanthene* derivative crystallised from alcohol in pale yellow needles, m.p. 272°. (Found : C, 75·6; H, 5·0. $C_{31}H_{25}O_5N$ requires C, 75·7; H, 5·0 per cent).

1-*Phenyl*-4-(*α-hydroxy-βββ-trichloroethyl*)-cyclo*hexane*-3 : 5-*dione*.—A mixture of chloral hydrate (1 g.), phenyldihydroresorcinol (2 g.), methyl alcohol (15 c.c.) and piperidine (4 drops) was kept at 25° for 24 hours. The solid, that separated out on dilution with water, was repeatedly crystallised from dilute alcohol, when pale yellow needles, m.p. 145-46°, were obtained. (Found : C, 50·0; H, 4·0. $C_{14}H_{13}O_3Cl_3$ requires C, 50·0; H, 3·8 per cent).

Oxide of 2 : 7-Diphenyl-4 : 5-diketo-1 : 2 : 3 : 4 : 5 : 6 :7 : 8-octahydrophenothioxin (?).—A mixture of thionyl chloride (2 c.c.) phenyldihydroresorcinol (2 g.) and dry benzene (15 c.c.) was refluxed on a water-bath for 6 hours till fumes of hydrochloric acid ceased to be evolved. Much of the benzene was removed and white prismatic needles, m.p. 216°, were obtained. The compound contained sulphur and gave blue colouration with concentrated sulphuric acid on slight warming. (Found : C, 71·2; H, 4·9. $C_{24}H_{20}O_4S$ requires C 71·2; H, 4·9 per cent).

Oxide of 2 : 2 : 7 : 7-tetramethyl-4 : 5-diketo-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenothioxin (?) was similarly obtained from dimethyldihydroresorcinol and thionyl chloride. It crystallised from benzene in pale yellow rhombohedra or from alcohol in pale yellow needles, m.p. 181-82°, and gave blue colour with concentrated sulphuric acid on slight warming. (Found : S, 10·1. $C_{16}H_{20}O_4S$ requires S, 10·4 per cent).

1 : 1-*Dimethyl-4-(α-hydroxy-βββ-trichloroethyl)* - cyclo*hexane-3 : 5-dione* was prepared from dimethyldihydroresorcinol and chloral hydrate. It crystallised from dilute alcohol in short, white needles, m.p. 120°. (Found : C, 41·3; H, 4·6. $C_{10}H_{13}O_3Cl_3$ requires C, 41·7; H, 4·5 per cent).

Furfuralbisdimethyldihydroresorcinol, obtained by the usual method from furfuraldehyde (2 g.), dimethyldihydroresorcinol (5·69 g.) and piperidine (4 drops), crystallised from dilute alcohol in white needles, m.p. 160°. (Found : C, 70·1; H, 7·1. $C_{21}H_{26}O_5$ requires C, 70·7; H, 7·2 per cent).

The *xanthene* derivative crystallised from alcohol as a black microcrystalline powder and did not melt up to 280°. (Found : C, 74·0; H, 7·0. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·0 per cent).

p-*Dimethylaminobenzal-bisdimethyldihydroresorcinol* crystallised from dilute alcohol, m.p. 114°. (Found : C, 72·7: H, 8·1. $C_{25}H_{33}O_4N$ requires C, 72·9: H, 8·0 per cent).

The *xanthene* derivative crystallised from alcohol in white short needles, m.p. 220°. (Found : C, 76·2; H, 7·8. $C_{25}H_{31}O_3N$ requires C, 76·3; H, 7·8 per cent).

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Studies in Vitamin C. Part II. The Vitamin C Contents of the Liver and Muscle of some Indian Fresh-water Fish.

By Mahendra Nath Rudra.

It has been shown by the author (*Biochem. J.*, 1936, **30**, 701) in a previous communication of this series that of all the parts of an animal generally used for edible purpose, the liver is the richest and the muscle the poorest in vitamin C, although considering all the tissues, the liver is not the organ richest in vitamin C. The concentration of the vitamin in the suprarenal cortex is greater than its concentration in the liver. However, on account of the very minute size of the suprarenal in proportion to the liver, the latter is a greater source of the vitamin. In the present investigation the vitamin C contents of the liver and muscle of some Indian freshwater fish have been determined.

Experimental.

The material was freed from all adhering tissues and bones as far as possible, and pressed between filter papers. 5-10 G. or as much of this as could be available were used in the determination of the vitamin. The vitamin C content was estimated by titration with 2 :6-dichlorphenol-indophenol after extracting with trichloroacetic acid as described in the previous communication.

The relative vitamin C values of the liver and muscle of different fish are given in Table I. The concentration of trichloroacetic acid in the final filtrate containing the vitamin, in our case, is about 5 %. McHenry and Graham (*Biochem. J.*, 1935, **29**, 2013) points out that 5 % trichloroacetic acid has a destructive effect on vitamin C. We have found that the vitamin is destroyed slowly but in about half an hour the destruction of the vitamin is not so appreciable as to warrant the prohibition of 5 % concentration of trichloroacetic acid in the final filtrate. In most cases the extraction of the vitamin and its titration are over in half an hour. The results of some experiments on the vitamin C content of the same extract just after extraction and 30 minutes after extraction are given in Table II. It will be seen that the vitamin C content does not diminish to a great extent after 30 minutes in trichloroacetic acid. Pure ascorbic acid in a solution of 5 % trichloroacetic acid concentration has also been titrated against the indophenol reagent. It has been found that the tritration values immediately after solution and after 15 and 30 minutes are identical.

Glick and Biskind (*J. Biol. Chem.*, **115**, 551) found that both the concentration and the amount of vitamin C per cell in bovine adrenal increase with the age of the fœtus until the calf stage while the concentration of the vitamin per cell in the adult gland is lower than the concentration of the vitamin in the calf gland. This is in agreement with the result found by us in the case of fish liver and muscle. It has been found that in the bigger fish of the same variety both the liver and the muscle are poorer in vitamin C than the liver and the muscle in the smaller fish. In Table III are given the vitamin C contents of the liver and muscle of fish of different weights of the same variety. These fish, for strict comparison, were collected from the same source. This result also agrees with the findings of Ghosh and Guha (*J. Indian Chem. Soc.*, 1935, **12**, 30) in the case of fruits. They found that with the gradual increase in the age of the fruit the ascorbic acid content decreased.

TABLE I.

Vitamin C Contents of Liver and Muscle of Different Freshwater Fish. (in mg./100 g.).

Name of fish.	Scientific name.	Vit. C Contents.	
Vern. name (Bengali)		Liver.	Muscle.
Rohit	*Labeo rohita*	160·0	20·0
(another sample)		66·5	6·8
Kalbosh	*Labeo calbosi*	57·3	11·2
Katla	*Catla catla*	29·6	7·0
(another sample)		41·9	9·2
Mrigal	*Cirrhina mrigala*	28·5	11·0
Hilsa	*Clupea ilisha*	48·0	27·7
Air	*Arius arius*	23·0	11·7
Bacha	*Clupisoma garua*	40·8	11·0
Boal	*Wallago attu*	16·0	6·0
Dhain	*Silonia silundia*	114·4	16·3
Pangash	*Pangasius pangasius*	23·0	12·5
Sharputi	*Barbus sarana*	58·4	16·4
Bhola	*Sciaena coitor*	59·1	14·1

TABLE II.

Vitamin C content of the same extract just after extraction and 30 minutes after extraction having a concentration of 5 % trichloroacetic acid (in mg./100 g.).

Name of material	Vit. C content	
	just after extraction.	30 mins. after extraction.
Liver	66·51	64·71
,,	57·28	56.6
,,	23·02	22·5

TABLE III.

Vitamin C content of the Liver and Muscle of Fish of different weights of the same variety (in mg./100 g.)

Name of fish.	Wt.	Vitamin C contents	
		Liver.	Muscle.
Labeo rohita	5·0 lbs.	66·51	6·8
,,	2·5	160·0	20·0
Catla catla	32·0	29·64	7·0
,,	1·2	40·26	8·6
,,	0·31	41·9	9·16

DISCUSSION.

A previous observation by the author (*loc. cit.*) about the vitamin C contents in the liver and muscle of animals has been confirmed in the case of freshwater fish obtained locally. The highest content of vitamin C (160 mg./100 g.) has been found in the liver of *rohit* (*Labeo rohita*) while the lowest (16 mg /100 g.) has been found in the liver of *boal* (*Wallago attu*). The highest vitamin C content (27·65 mg./100 g.) of muscle has been found in the case of *Clupea ilisha*, the lowest being in the case of *Wallago attu*. It has also been observed that a concentration of 5 % trichloroacetic acid in the final extract has, for practical purposes, very little destructive effect on the vitamin C content provided the extraction and titration with the indophenol reagent is over in about half an hour. The particular tissues of the younger fish are richer in vitamin C than those of a bigger fish of the same variety.

In conclusion I wish to thank Dr. S. L. Hora of the Zoological Survey of India for kindly supplying me with the scientific names of most of the varieties of fish used in this investigation.

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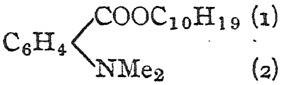
Studies on Optical Activity and Chemical Constitution. Part III. Optically Active Acids and Bases.

By Mahan Singh and Manohar Singh.

Rule (*J. Chem. Soc.*, 1927, 54) has shown that optically active menthyl and *sec*-β-octyl esters of acetic acid and *ortho*-substituted benzoic acids, containing basic substituents, have relatively low rotatory powers, which rise when the compounds are examined in the form of their hydrochlorides. The following values are recorded in the case of free amines and their hydrochlorides (*Trans. Faraday Soc.*, 1930, 330).

$Me_2N{\cdot}CH_2{\cdot}COOC_{10}H_{19}$



$$C_6H_4\begin{cases} COOC_{10}H_{19} & (1) \\ NMe_2 & (2) \end{cases}$$

Amine, $[M]_{5461} = -201°$ Amine, $[M]_{5461} = -250°$

Hydrochloride, $[M]_{5461} = 204$ Hydrochloride, $[M]_{5461} = -292$

It has been suggested that in the case of monosubstituted acetic acids the structural changes occur at a considerable distance from the optically active group and the effect on the rotatory power is, therefore, small.

This paper deals with the preparation and the optical rotatory powers of 2′-, 3′- and 4′-dimethylaminocamphoranilic acids. The following table records the rotatory powers of 2′-camphoranilic acids.

TABLE I.

$[\alpha]_D$ in methyl alcohol.

CO_2H *	OH‡	NMe_2	OMe‡	Cl†	Me†	H†
−157°	−12·6°	0°	9·0°	18·7°	50·5°	57·5°

It would be seen that the dimethylamino group has lowered the rotation of the original compound considerably.

2′-Dimethylaminocamphoranilic acid is an example of an optically active amino-acid, and the substance was examined in the presence of an equivalent amount of alkali and also with an equivalent amount of hydrochloric acid. It has a slight positive rotation in the neutral medium, which increased very little when examined in the presence of alkali, but the rotatory power increased enormously when an equivalent weight of the acid was added.

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* *J. Chem. Soc.*, 1925, 1966. † *Ibid.*, 1927, 1995. ‡ *Ibid.*, 1930, 1207.

Ths following values with and without the addition of hydrochloric acid will be found interesting.

TABLE II.

λ=	5893	5780	5461	4359
Neutral medium	0°	6·2°	8·12°	18·70
1 mol HCl	55·52	57·02	68·52	118·54

The marked changes in the rotatory power may be attributed to the fact that the group of electrons which gives rise to optical rotatory power is considerably modified (*cf.* J. Liquier Milward, *Ann. Physique*, 1927, **8**, 121).

The dimethylamino group in the 4′- position has, however, raised the rotatory power of the original compound but not to the extent as was expected. This effect of the alkylamino group in the 4′-position has already been shown in the case of dimethyl and diethylaminophenyliminocamphors (*J. Indian Chem. Soc.*, 1935, **12**, 219, 768):

I[1] Br[1] OMe[2] Me[3] Cl[3] NMe_2 OH[2] COOH[4]

The 4′- dimethylamino acid was also examined in the presence of an equivalent amount of hydrochloric acid and then in the presence of an equivalent amount of caustic alkali. In the first case $[\alpha]_D$ fell from 62·37 to 40·02°, but in the second case there was a slight increase, $[\alpha]_D$ being 63·69°. It appears that the ionisation of an active carboxylic acid leads to a smaller change in rotatory power than the ionisation of an active base.

The rotatory powers of these compounds have been determined in three solvents, *i.e.*, methyl alcohol, ethyl alcohol and acetone. The

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[1] *J. Chem. Soc.*, 1928, 2410. [2] *Ibid.*, 1930, 1201. [3] *Ibid.*, 1927, 1995.
Ibid., 1925, 1996.

4′-dimethylamino acid shows simple dispersion as by plotting $\frac{1}{a}$ against λ^2, exact straight lines are obtained, but the rotatory dispersion of 2′-dimethylaminocamphorophenylimide is complex in all the three solvents.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Aminodimethylanilines.—Camphoric anhydride and the amine (equal mols.) were heated together with a little fused sodium acetate in an oil-bath at 125-130° for 3 hours. The product was dissolved in alcohol and precipitated with water, when dark grey solid was precipitated. It was extracted with dilute solution of caustic soda to remove any imide formed. The filtered solution was then acidified with acetic acid till a slight turbidity was produced. It was kept overnight when a grey colouring matter settled. It was removed by filtration through a double filter paper and the filtrate was acidified. The solid mass, thus obtained, was crystallised from alcohol.

4′-Dimethylaminocamphoranilic Acid was crystallised from alcohol in white microcrystalline mass, m.p. 193° after darkening at 187°. It is soluble in the usual organic solvents but insoluble in benzene and water. (Found: N, 9·07. $C_{18}H_{26}O_3N_2$ requires N, 8·80 per cent).

3′-Dimethylaminocamphoranilic Acid.—All attempts to crystallise it were unsuccessful. It was, therefore, purified by repeated dissolution in alkali and precipitation with an acid. It was obtained as a greyish white amorphous mass, darkening at 90°, shrinking at 100° and melting at 120°. (Found: N, 9·0. $C_{18}H_{26}O_3N_2$ requires N, 8·80 per cent).

2′-Dimethylaminocamphoranilic Acid was crystallised from alcohol in colourless needles, m.p. 152-53°. (Found: N, 9·0. $C_{18}H_{26}O_3N_2$ requires N, 8·80 per cent).

*Camphoro-*o*-dimethylaminophenylimide.*—The residue left on the filter paper after treatment with dilute ammonia was crystallised from dilute alcohol (charcoal) as microcrystalline powder, m.p. 149°. (Found: N, 9·45. $C_{18}H_{24}O_2N_2$ requires N, 9·33 per cent).

TABLE III.

Specific rotations.

	Conc./25 cc.	$[\alpha]_D$	$[\alpha]_{5780}$	$[\alpha]_{5461}$	$[\alpha]_{4354}$
4′-Dimethylaminocamphoranilic Acid.					
MeOH	0·2005 g.	69·82°	74·81°	92·26°	183·28°
EtOH	0·2004	62·37	66·11	78·59	158·43
Me_2CO	0·1999	54·44	55·65	68·78	137·00
3′-Dimethylaminocamphoranilic Acid.					
MeOH	0·2510	55·7	59·7	66·7	
EtOH	0·2015	37·8	39·0	49·0	
Me_2CO	0·2525	27·7	34·6	39·6	
2′-Dimethylaminocamphoranilic Acid.					
MeOH	0·2005	0	6·2	8·72	18·7
EtOH	0·3004	0	0	0	18·0
Me_2CO	0·2006	−9·97	−16·82	−17·44	−22·43
Camphoro-o-dimethylaminophenylimide.					
MeOH	0·2003	14·35	17·47	26·83	43·68
EtOH	0·2005	11·22	14·34	21·82	39·90
Me_2CO	0·2530	23·7	27·7	41·5	56·8

The readings were taken in a 2 dcm. tube and the temperature during all these readings was 25-26°.

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A New Method for the Separation of Lead from Copper and their Subsequent Estimations.

By K. M. Sil, G. C. Roy and P. N. Das-Gupta.

The respective actions of hydrogen peroxide and ammonia on solutions of lead and copper nitrates give rise to a new method of separation of lead from copper. Hydrogen peroxide and ammonia precipitate lead quantitatively from a solution of its nitrate, in the form of a definite compound $Pb_5O_7, 3H_2O$ (Das-Gupta, Roy and Sil, *J. Indian Chem. Soc.*, 1928, **5**, 657), whereas the reagents have got no action on copper nitrate solution, except the usual formation of a deep blue solution.

It has been found that to separate copper completely, lead requires to be precipitated twice, as in its first precipitate a small amount of copper remains adsorbed. The lead precipitated a second time, in one set of experiments, is taken in a gooch, dried and weighed as $Pb_5O_7, 3 H_2O$ and in another set of experiments it is transformed into PbO and weighed as such (Sil, *J. Indian Chem. Soc.*, 1933, **10**, 137). In the combined filtrates from the first and second precipitations of lead, copper is estimated iodometrically after decomposing hydrogen peroxide left in the filtrate by boiling with nitric acid.

EXPERIMENTAL.

Solutions of lead and copper nitrates were separately made by dissolving about 16·5 g. of lead nitrate and about 24 g. of copper nitrate in 500 c.c. of water respectively and in these solutions lead was estimated as $Pb_5O_7, 3 H_2O$ and also as PbO and copper was estimated iodometrically. The precipitation of lead from the lead nitrate solution in presence of nitric acid and the nature of the precipitate, nitric acid is required to dissolve the first lead precipitate. In this study it has been found, that lead can be estimated as $Pb_5O_7, 3H_2O$ in the solution, which contains concentrated nitric acid up to the extent of 0·25 c.c. per 100 c.c. Where the amount of the free acid is greater, the volume of the solution should be so increased by adding water that it may not contain more than 0·25 c.c. of concentrated HNO_3 per 100 c.c.

Separation of Lead from Copper and their Estimations.

Measured volumes of lead and copper nitrate solutions were taken and mixed together, the mixture was diluted to a volume of 100 c.c. with water and one or two drops of dilute nitric acid were added. In this, lead was precipitated by requisite amount of hydrogen peroxide and excess of concentrated ammonia. For every 5 c.c. of the lead nitrate solution, 2 c.c. of 3% hydrogen peroxide and 2 c.c. of concentrated ammonia were added and for every 5 c.c. of the copper nitrate solution in a volume of 100 c.c., 2 c.c. of concentrated ammonia were also added. The precipitate of lead with the blue solution of copper was then heated over a water-bath for 20 minutes; by this time the precipitate attained a crystalline nature. The crystalline lead precipitate was then washed by decantation with hot ammoniacal water (3 or 4 c.c. of conc. NH_4OH in 50 c.c. of water) 3 or 4 times on a filter till the wash-water was colourless. The filtrate was taken in a basin of 500 c.c. capacity, when the amount of copper present was small. In case of the presence of large amounts of copper, the filtrate was taken in a 500 c.c. measuring flask. The filter was then washed into the beaker in which the lead was precipitated, first by a jet of hot water, then pouring on it a few drops of hot dilute nitric acid and hydrogen peroxide and again washing with a jet of hot water. The lead precipitate in the beaker was then dissolved by adding a small quantity of hot dilute nitric acid and hydrogen peroxide and then heating. The solution was then cooled and diluted with water to a volume such that it did not contain more than 0·25 c.c. of free concentrated HNO_3 per 100 c.c. In this solution the precipitation of lead was carried a second time as before and the lead precipitate was filtered through a Jena glass silica-bed crucible, after washing it by decantation with hot ammoniacal water 3 or 4 times, till the filtrate was free from copper and nitrate. The presence of copper was tested first; when copper was found absent, the test for nitrate was also found negative. This filtrate was mixed with the first filtrate and was kept for the estimation of copper. The precipitate on the crucible was finally washed with a little absolute alcohol and dried at 110°-120° for half an hour and weighed as $Pb_5O_7, 3H_2O$.

Either the whole or an aliquot part of the mixed filtrates, according to the amount of copper present, was acidified with nitric acid and evaporated to a volume of not more than 100 c.c. and then boiled for 10 minutes to decompose the hydrogen peroxide present. The solution was cooled and was made alkaline with excess of ammonia, then acidified with acetic acid and 3 g. of potassium iodide added. The liberated iodine was titrated by *N*/10-sodium thiosulphate solution, which was standardised against *N*/10-copper sulphate solution prepared by dissolving exactly 6·2427 g. of $CuSO_4$, $5H_2O$ (Merck's reagent quality) in 500 c.c. of water. From this titration the amount of copper present was calculated.

Several estimations were made, with mixtures of lead and copper nitrate solutions in different proportions, in the way as stated above, the results of which are given in Table I.

TABLE I.

$Pb(NO_3)_2$.	$Cu(NO_3)_2$.	H_2O_2.	Conc. NH_4OH.	Pb_5O_7, $3H_2O$.		Copper	
				Found.	Present.	Found.	Present.
5 c.c.	1 c.c.	2 c.c.	3 c.c.	0·1205 g.	0·1200 g.	0·01310 g.	0·01315 g.
50	1	20	21	1·2060	1·2000	0·01303	,,
1	50	2	21	0·0240	0·0240	0·6579	0·6575
5	50	2	22	0·1200	0·1200	0·6579	,,
5	10	2	6	0·1203	,,	0·1313	0·1315
10	5	4	6	0·2402	0·2400	0·0656	0·06575
5	20	2	10	0·1205	0·1200	0·2629	0·2630
20	5	8	10	0·4810	0·4800	0·0658	0·06575
10	30	4	12	0·2403	0·2400	0·3941	0·3945
30	10	12	16	0·7242	0·7200	0·1313	0·1315
5	5	2	6	0·1203	0·1200	0·0658	0·06575
10	10	4	10	0·2405	0·2400	0·1316	0·1315

Considering the presence of ammonium nitrate in the solution for the precipitation of lead a second time, the second lead precipitate was filtered, dried and transformed to PbO and weighed as such. Several estimations carried in this way are also given in Table II.

TABLE II.

*$Pb(NO_3)_2$.	$Cu(NO_3)_2$.	H_2O_2.	Conc. NH_4OH.	PbO		Cu	
				Found.	Present.	Found.	Present.
25 c.c.	25 c.c.	10 c.c.	20 c.c.	0·5500 g.	0·5515 g.	0·3286 g.	0·3288 g.
10	40	4	20	0·2200	0·2206	0·5238	0·5260
40	10	16	20	0·8828	0·8824	0·1310	0·1315
2	5	2	4	0·04410	0·04412	0·06579	0·06575
5	2	2	4	0·1107	0.1103	0·0263	0·0263
5	5	2	6	0·1100	0·1103	0·0656	0.06575
10	10	4	10	0·2210	0·2206	0·1313	0·1315

* A different lead nitrate solution.

In conclusion we are much thankful to Principal Dr. D. N. Mallik and Prof. J. C. Das of Carmichael College, Rangpur, for giving us facilities and encouragement to conduct this work in the Chemical Laboratory of the College.

CHEMICAL LABORATORY,
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Estimation of Small Quantities of Arsenic in Medicolegal Cases.

By D. N. Chatterji, K. R. Ganguly and M. Z. Faruqi.

In medicolegal investigations of arsenic poisoning cases, it is of importance to determine the quantity of arsenic in viscera and other articles, submitted for analysis.

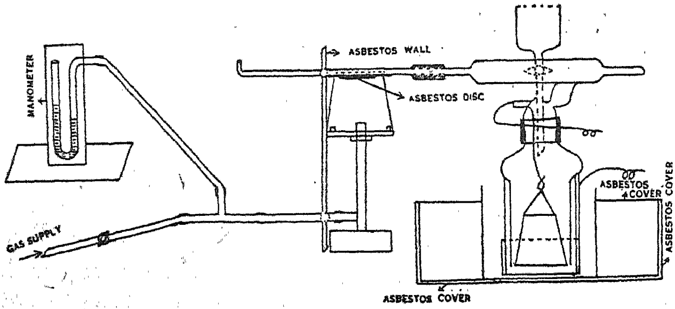
In our experience, the destruction of organic matter is best done by slightly modified Bang's method (*Analyst*, 1925, **50**, 5). We also tried the destruction of organic matter by Fresenious-Babo method ("Royal Commission on Arsenical Poisoning, Minutes on Evidence and Appendices," 1903, XI, 223), invariably a loss of arsenic due to volatilisation during the process of removing nitric acid, however, carefully it is done.

EXPERIMENTAL.

The process adopted by us is as follows. About 50 g. of the substance were taken in a silica Kjeldahl flask; spirit (if used as preservative), or water, if present, should first be removed before putting the substance into the flask. 8·0 ml. of strong H_2SO_4 were added, followed by 2·0 ml. of strong HNO_3. The flask was then gently heated on a wire gauze, and HNO_3 was dripped into the flask from a separating funnel with a bent stem. In about 5 to 6 hours' time the digestion was complete, and a clear liquid was obtained. The major portion of the nitric acid remaining in the liquid was got rid of by heating it until white fumes appeared. The last traces of the nitric acid were removed by boiling the liquid in the flask with 10 ml. of saturated ammonium oxalate or saturated urea solution. We have found that without this treatment traces of HNO_3 remain in the liquid, which interfere with the estimation of arsenic.

When the quantity of arsenic is small, two methods for its determination are applicable, *viz.*, the Gutzeit and the Marsh-Berzelious method. We find it more convenient to adopt the electrolytic Marsh-Berzelious method (" Royal Commission Report on Arsenical Poisoning," 1903, p. 4) using platinum electrodes with certain modifications as stated below.

The platinum gauze was discarded and the tube was heated directly by putting it just above the reducing zone of the flame. The gas pressure, which is indicated by a manometer having one end open and the other connected to the gas conducting tube and containing some coloured water, was adjusted by a pinch-cock. A difference of one inch in the two arms of the manometer was maintained. The temperature of the water in the cooling bath was not allowed to rise above 10°. As the atmospheric shade temperature in Agra generally varies from 45° to 2° during the year, the following device was employed to maintain the required temperature of the bath which was kept fed with ice. In summer when the atmospheric temperature is pretty high, the water in the bath was protected from being heated up by the air temperature, by covering the outside walls and the top of the bath, except the portion occupied by the electrolytic glass cell, with asbestos sheets. In winter the heat developed within the electrolytic cell was allowed to radiate into the cool outside atmosphere by removing the asbestos sheets. The Marsh's tube in which the mirror was formed was placed on a small circular asbestos disc having a hole at the centre for the flame and resting on the chimney of the gas burner in order to prevent heat being conducted through the wall of the chimney with radiation into the atmosphere. If the heat be not sufficient, the arsenuretted hydrogen is not completely decomposed. It is also necessary in the hot weather of Agra to prevent the overheating of the part of the tube where the arsenic is to deposit. This is done by placing an asbestos screen vertically between the chimney of the burner and the part of the tube where the arsenic mirror is to form, the tube passing through a hole in the asbestos screen.



It is extremely important that before introducing the solution, obtained after destruction of the organic matter into the Marsh's apparatus, the arsenic contained in it should be reduced completely into the arsenious state. We found that sulphurous acid is not satisfactory for this purpose. The reduction of arsenic by it is not only incomplete, but uncertain in extent. Reduction with a solution of arsenic was accomplished by digesting the solution on a water-bath with a mixture of pyrogallic acid solution and sulphurous acid. This was done with respect of each portion of the solution introduced into the Marsh's apparatus and immediately before starting the test, ensuring at the same time that no excess of sulphurous acid remained in the solution. Unless the reduction of arsenic be done immediately before the test, some of the reduced arsenic is again transformed into its higher state of oxidation. The qualities of the reagents used by us were 2·0 c.c. of 0·5% pyrogallic acid solution and 4·0 c.c. of sulphurous acid. By this process quite good results were obtained, without previous distillation of the solution as has been recommended in the case of dyestuffs (*Analyst*, 1930, **55**, 103). It was also found unnecessary to prepare the standard arsenic solution by treatment of the same kind of material as under examination after adding to it a a known quantity of As_2O_3 as recommended by some authorities (Royal Commission Report on Arsenic Poisoning, 1903, p. 10). We prepared the standard solution by directly dissolving arsenious acid.

The following table shows the advantage of reducing the arsenic in the solution for test into arsenious state by a mixture of pyrogallic and sulphuric acids in the manner stated above.

Nature of substance to which a weighed quantity of As_2O_3 added and the soln. for test prepared after destruction of the organic matter by the modified Bang's method.	The entire liquid after digestion reduced with H_2SO_3, made up to a known volume and further diluted, if necessary for Marsh's test.		Only the portion introduced into the Marsh's apparatus reduced with H_2SO_3 acid, just before the test		Only the portion introduced into the Marsh's apparatus reduced with pyrogallic and sulphurous acids, just before the test.	
	Amt. of As_2O_3 taken in the electrolytic apparatus.	The standard As_2O_3 mirror with which the mirror from the soln. to match.	Amt. of As_2O_3 taken in the electrolytic apparatus.	The standard As_2O_3 mirror with which the mirror from the soln. to match.	Amt. of As_2O_3 taken in the electrolytic apparatus.	The standard As_2O_3 mirror with which the mirror from the soln. to match.
Goat's viscera	0·03 mg.	0·007 mg.	0·0036 mg.	0·002 mg.	0·0036 m.g.	0·004 mg.
,,	0·007	0·006	0·006	0·005	0·006	0·006
,,	0·016	0·006	0·0064	0·004	0·0064	0·006
,,	0·020	0·006	0·004	0·003	0·004	0·006
,,	0·013	0·006	0·004	0·002	0·004	0·004
Arsenic-free human stomach	0·021	0·006	0·0062	0·003	0·0062	0·006

The chemicals used in the test were all free from arsenic

All the standard mirrors were prepared from the same stock solution, which before introduction into the electrolytic apparatus was treated with a mixture of pyrogallic and sulphurous acid solutions.

AGRA GOVERNMENT LABORATORY,

AGRA.

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Studies in the Coagulations of Colloids. Part XV. New Aspecs of Gold Sol Coagulation.

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In respect of the kinetic studies of its coagulation, the wide variety of the methods and conditions of its preparation, the correlation of some of the chief physical constants, especially optical properties, with the size and shape of the particles etc., the gold hydrosol is amongst the most well investigated of colloid systems, since practically the beginning of the growth of the subject at the hands of a number of well known workers. It *most nearly* fulfils the requirements of a monodisperse sol. The positions, the intensities of its characteristic absorption bands, and especially the marked variations in them during coagulation have especially favoured the selection of the gold sol for accumulating data in relation to the predictions of the theories for the kinetics of coagulation and allied changes, as developed especially by Smoluchowski (*Z. physikal. Chem.*, 1917, **92**, 129) and Freundlich ("Colloid and Capillary Chemistry," 1926, pp. 442-450) and others.

This has produced a mass of experimental results which have in the main confirmed the requirements of the theory in the region of *rapid* coagulation. Previous papers in this series (Joshi and co-workers, *J. Indian Chem., Soc.*, 1933, **10**, 329, 599 ; 1934, **11**, 133, 555, 573, 797 ; 1936, **13**, 141, 217, 309, 311, 439 ; *J. chim. phys.*, 1935, **32**, 455 ; *Proc. Acad. Sci. U. P.*, 1935, **5**, 41 ; *Bombay Univ. Journ.*, 1935, **4**, 140 ; *Kolloid Z.*, 1936, **76**, 145 : *Current Science*, 1936, **4**, 481, 870) on the *slow* coagulations of a number of sols and dilute emulsions (which were presumably *polydisperse*,) have shown, however, that departures from the theory, arise chiefly because Smoluchowski (*loc. cit.*) has assumed tacitly that even in the *slow* region, coagulation is but a *time continuous* coalescence of the primaries. It was of interest therefore, to examine the behaviour of the gold sol from the sandpoint of this deduction in regard to the deficiency in the current theories. It will be seen that the results now reported confirm the criticism developed in this series.

EXPERIMENTAL.

The gold sol was prepared according to a method due to Zsigmondy (*Z. Electrochem.*, 1906, **12**, 721). 10 C. c. of 0·38% gold chloride solution were added to 200 c. c. of twice distilled water and made alkaline by means of 10 c. c. of 0·2 *N*-potassium carbonate solution. The solution was then heated to the boiling point and 5 to 6 c. c. of 0·3% formalin were added drop by drop with continuous shaking. A fine, transparent red sol was obtained, which was boiled for a short time. Only Jena vessels were used during this work. The sol was next dialysed against repeated changes of redistilled water, till the dialysate was free from the chloride. The course of the coagulation was studied by observation of the corresponding change of the viscosity and of refractive index. The course of the sol during coagulation, relative to that of water was measured by Scarpa's method with modifications described previously (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329). The suction applied was kept constant at 29·35 + 0·05 cm. of water. The observation of the water level being made with a low power telescope. The temperature of the thermostat was 80 + 0·05°. Equal volumes of the sol (10 c. c.) and of coagulating solution, which had already attained the thermostat temperature were mixed in the Scarpa tube at a known time and the viscosity of the mixture measured at suitable intervals till visible flocculation set in. The concentration of the coagulant is expressed in term of millimols (m. m.) of the electrolyte used *in the coagulating mixture*. The general procedure and precautions taken are described in an earlier paper (Joshi and Viswanath, *loc. cit.*). Of the colloids studied previously (*loc. cit.*) the viscosity of the gold sol approached most nearly that of water. Further more, the viscosity variations consequent on coagulation with dilute coagulants were small. These have not been shown in Fig. 1.

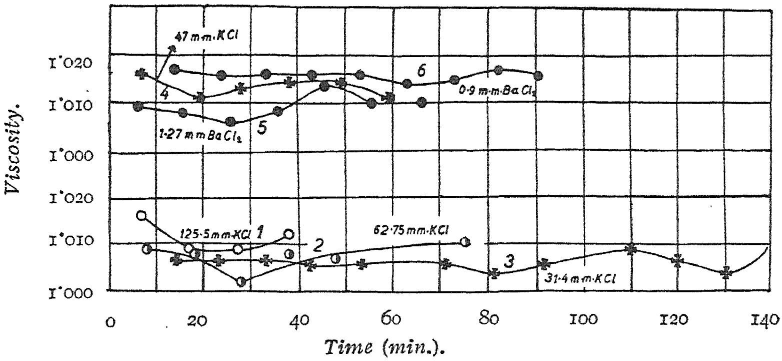
Thus refractive index for the D line was measured during coagulation by means of a Pulfrich refractometer as described previously (Joshi and Jaya Rao, *J. Indian Chem. Soc.*, 1936, **13**, 141). The results have been shown graphically in Figs. 1 and 2. They are but a few typical curves selected from a much greater number of viscosity—time and refractive index—time curves distinctive of numerous coagulations actually examined.

DISCUSSION.

The general indication of the viscosity—time curves in Fig. 1 confirms the conclusion drawn previously from independent data accumulated in these laboratories, *viz.*

(*a*) Contrary to the tacit assumptions in general made by colloid chemists a coagulation does not always produce a net *rise* in the viscosity of the coagulating mixture. For example, in the coagulation represented by Fig. 1, curve 1, flocculation had set in immediately on the addition of the electrolytes ; the corresponding viscosity, however, shows an overall decrease.

FIG. 1.

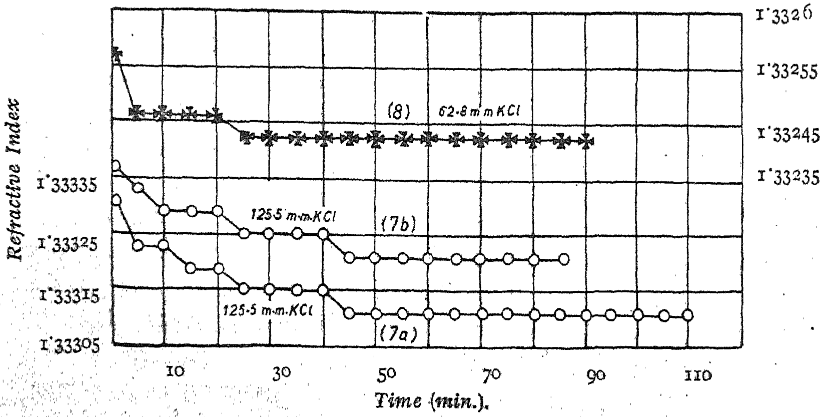


(*b*) One of the early stages in a coagulation is usually though not invariably characterised by a diminutlon of viscosity, followed by a subsequent rise.

(*c*) The progress of the viscosity change during especially a *slow* coagulation is discontinuous with respect to the time of coagulatton (Joshi and co-workers, *loc. cit.*). Gallecki (*Kolloid Z.*, 1925, **36**, 154 *et. seq.*) in the course of a comprehensive study of the physicochemical properties of the gold hydrosol, has observed the occurence of minima on the viscosity—time curves in numerous coagulations. Whilst our results are in agreement with this, we are of the opinion that these minima are but a part of a wider continuous but *slow* coagulation, *viz.*, it is not time continuous but, *zonal*, *i.e.*, proceeds through a series of stages corresponding to the breaks or discontinuities on the coagulation—time curves. Gallecki (*loc. cit.*) has made interesting observations of conditions for the characteristic colour change, red to blue, and the corresponding viscosities. As has also been found that due to prolonged '*ageing*' the viscosity falls to a minimum and ascribes it to insipient precipitation. Exposure to ultraviolet has the *opposite* effect. It is further suggested that the first minimum on the viscosity—time curves corresponds to the transformation, red to blue, during electrolytic coagulation. Our results, however, are not in agreement with this. In coagulations represented by Fig. 1, curves 3 and 6, visible flocculation was observed within 140 and 95 minutes respectively, the mixture remained violet for appreciably long periods within which the viscosity remained practically constant. No sensible change in the colour was observed even in later stages of the above coagulations; the viscosity—time curves, however, show a series of maxima and minima. In coagulations corresponding to Fig. 1, curves 2, 4, and 5, there was flocculation within about 1 hour; the sol had, however, changed to violet almost immediately on the addition of the electrolyte and no special colour change was noticed, corresponding to either the first or any of the subsequent minima on the viscosity—time curves. It follows, therefore, in agreement with earlier results with different colloid systems (Joshi and Jaya Rao, *J. Indian Chem. Soc.*, 1933, **10**, 254) that, than those dependent on merely colour or turbidity changes, the viscosity measurements might under certain conditions be more sensitive to micellar reactions, and therefore, better adapted to bring out the characteristic '*zonal*' character of a *slow* coagulation.

The results of the determination of n_D the refractive index during coagulations with solutions of potassium chloride shown in Fig. 2, fully confirm the above deduction about the '*zonal effect*' constituting a *slow* coagulation. A number of observations were made

FIG. 2.



with differently concentrated solutions of sodium chloride, barium chloride and gold chloride, as also of potassium chloride of strengths other than those reported here. The principal feature of all these coagulation—time curves were completely analogous to those shown by those in Fig. 2. Curves 7a and 7b, Fig. 2, refer to n_D-time changes under conditions as identical as possible. It is seen that although the details are not reproducible, the identity of the general form in revealing the occurrence of '*zones*' is definite. The results with sodium chloride showed a much greater number of '*zones*', *i.e.*, the discontinuities, and that the *net* change in n_D, the refractive index was less than with potassium chloride. Also in agreement with results reported elsewhere on colloid manganese dioxide (*Kolloid. Z.*, 1936, **76**, 145), the net diminution in the last quantity was small for every small concentrations of the coagulant. In view of the very large amount of experimental work reported in the literature on the optical properties of gold sols, both when pure and subjected to coagulation, it is not a little interesting that no observations, *earlier than these*, appear to have been made about the '*zonal*' variation of n_D during coagulations in the *slow* region. As observed in similar studies of n_D variations during coagulations, the '*zonal effect*' tends to disappear for very *slow* and also during rapid coagulations.

SUMMARY.

Changes in the viscosity and n_D, the refractive index in the Zsigmondy gold sol during coagulations by NaCl, KCl, $BaCl_2$ and (for n_D) $AuCl_3$ have been examined. In agreement with earlier findings it has been concluded that a net rise of viscosity is not necessarily a concomitant of coagulation. The two changes might be even in opposite senses. Contrary to the results of Galecki, the occurrence of minima on the viscosity—time curve is independent of the colour change, red to blue, during coagulation. The progress of viscosity change has been found to be *zonal* or discontinuous with respect to coagulation time in the *slow* region. The refractive index measurements also show this *zonal effect* : this last is most pronounced in moderately *slow* coagulations.

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INDEX OF AUTHORS

PAGE

ACHARYA, Harendra Kumar.—Properties of activated sugar charcoal coated with various substances. Part I. Liberation of acid and alkali by the action of neutral salts in relation to the surface charge 723

AGARWAL, Radha Raman.—Chemical examination of *Cuscuta reflexa*, Roxb. Part IV. Isolation of a new yellow flavone colouring matter from the seeds 531

AGARWAL, Radha Raman and Sikhibhushan DUTT.—Chemical examination of *Cuscuta reflexa*, Roxb. Part. III. The constituents of the oil from the seeds 264

ALIMCHANDANI, Rupchand Lilaram.—See Narshinh Muljibhai SHAH.

BAGCHI, Phanindra Nath.—See Duhkhaharan CHAKRAVARTI.

BAMJI, C. N.—See A. N. MELDRUM.

BANERJEE, Bhawani Charan.—See Duhkhaharan CHAKRAVARTI.

BANERJEE, Jiban Krishna.—See Satya Prasad ROYCHOUDHURY.

BANERJEE, Pares Chandra.—Use of vanadous sulphate as a reducing agent. Part II. Estimation of chlorates, nitrates and persulphates 301

BARDHAN, T. P.—See J. K. CHOWDHURY.

BASU, Kali Pada and Sati Prasad MUKHERJEE.—Action of dyestuffs and other substances on milk dehydrogenase. Identity of Schardinger enzyme with xanthine oxidase ... 11

BASU, Kali Pada and Madhab Chandra NATH.—On the proteinase in the milky juice of *Calotropis gigantea* Its purification and activation by ascorbic acid and glutathione ... 34

BASU, N. M. and S. R. MAITRA.—Investigation on the effects of humidity and high temperature on the NH_2- content of different samples of rice 255

BASU-MALLICK, Hariprasad.—See Sisir Kumar GUHA.

PAGE

Bedi, Sant Singh and Kartar Singh Narang.—Quinazolines. Part IV. 253

Bhabak, Krishnadhan.—See Jnanendra Nath Mukherjee.

Bhatia, V. S.—See M. A. Hamid.

Bhatnagar, S. S., A. N. Kapur and P. L. Kapur.—A magnetic study of colour changes in cobalt chloride. Part II. ... 489

Bhatnagar, S. S., A. N. Kapur and M. L. Puri.—Adsorptive properties of synthetic resins 679

Bhatnagar, S. S., M. B. Nevgi and R. L. Sharma.—Diamagnetic susceptibilities of tin in di- and tetra-valency states ... 273

Bhatnagar, S. S. and N. G. Mitra.—A critical examination of Pascal's value for the magnetic susceptibility of the CH_2-group 329

Bhattacharya, Abani K.—Influence of dilution on the molecular refractivities of complex cyanides and cobaltammines 284

Bhattacharya, Rama Ranjan.—See Susil Kumar Ray.

Bhattacharyya, Promode Behari and Kalipada Ganguli.—On the physico-chemical properties of electrodialysed gels of silica, alumina, ferric hydroxide and their mixtures. Part I. Ion exchange 204

——On the physico-chemical properties of electrodialysed gels of silica, alumina, ferric hydroxide and their mixtures. Part II. Moisture retention capacity of the gels saturated with different cations 547

Bhojraj, Moreshwar Govind.—See Andrew Norman Meldrum.

Bokil, K. V.—Oxidation of acetyltetrahydroquinoline sulphonic acids 404

Bose, Prafulla Kumar and Nirmal Chandra Guha.—On some synthetic compounds related to atophan 700

Bose, Prafulla Kumar and Anil Chandra Roy.—The constitution of ayapanin 586

Chakravarti, Duhkhaharan and Bhawani Charan Banerjee.—Synthesis of coumarins and chromones from halogenated and nitro-cresols 619

Chakravarti, Duhkhaharan and Phanindra Nath Bagchi.—Synthesis of coumarins and chromones from 4-chloro- and 4-bromo-1-naphthol 649

——On the limited applicability of Kostanecki's reaction 689

PAGE

CHATTERJEE, Nirmalapada.—Investigations on cod liver oil emulsions. Antagonism of emulsifying agents ... 563

CHATTERJEE, Nripendra Nath.—Spiro-compounds. Part I. A new route to spiro-compounds. Synthesis of *cyclo*hexane-spiro-*cyclo*pentane 536

——Spiro-compounds. Part II. Ring transformation in spiro-compounds from 4-methyl*cyclo*hexanone. A new synthesis of cadalene 588

——Synthesis of diphenyl acetates 593

——Phenanthrene from 9-hydroxyphenanthrene (A note) ... 659

CHATTERJI, D. N., K. R. GANGULY and M. Z. FARUQI.—Estimation of small quantities of arsenic in medico-legal cases ... 751

CHAUDHURY, Subodh Govinda and Jyotirmoy SEN-GUPTA.—On the relation between peptisation of a precipitate and its electrokinetic potential 670

——See also Jnanendra Nath MUKHERJEE.

CHOPRA, Narindra Nath and Jnanendra Nath RÂY.—Methoxy-oxypalmatine 478

CHOWDHURY, Dwipendra Chandra.—See Anukul Chandra SIRCAR.

CHOWDHURY, J. K. and T. P. BARDHAN.—Molecular size of cellulose from different sources. Part I. 240

——Measurement of molecular size of cellulose from different sources by surface tension. Part II. 294

DAS, Ahsutosh and Rajendralal DE.—Negative ferric hydroxide sol. A modified method of its preparation 197

DAS-GUPTA, Hirendra Nath.—Studies in organo-arsenic compounds. Part III. 305

DAS-GUPTA, P. N.—See K. M. SIL.

DAS-PURKAYÂSTHA, B. C.—See M. GOSWAMI.

DE, Rajendralal.—See Ashutosh DAS.

DE, S. C. and P. C. RAKSHIT.—Synthesis in the pyrazolone series. Part IV. Action of aminoguanidines on β-ketonic esters and β-diketones 509

DE, S. S.—See B. N. GHOSH.

DESAI, R. D. and M. A. WALI.—Dihydroresorcinols. Part IV. The condensation of phenyldihydroresorcinol with aromatic aldehydes 735

PAGE

DEY, B. B. and T. K. SRINIVASAN.—Studies in the cotarnine series. Part VII. Action of sulphuric acid on cotarnine : Formation of methylene*bis*phenol-betaine of 2-methyl-6 : 7-dihydroxy-8-methoxy-3 : 4-dihydro*iso*quinolinium hydroxide 337

DEY, B. B. and (Miss) P. Lakshmi KANTAM.—Studies in the cotarnine series. Part VI. Condensation of cotarnine with phosgene 281

DEY, B. B., S. RENGACHARI and M. V. SITHARAMAN.—Peroxidases. Part III. A potentiometric method of estimating their activity 390

DHAR, N. R. and S. K. MUKERJI.—Available nitrogen in tropical soils. Part I. 21

——New aspects of nitrogen fixation and conservation in soil. Part I. 155

——Denitrification in sunlight and its retardation 555

DHAR, N. R. and S. P. TANDON.—Oxidation of nitrites to nitrates in sunlight 180

DHAR, N. R. and Ch. I. VARADANAM.—Preparation and properties of highly concentrated sols. Part V. Stannic hydroxide sols 602

——See also C. C. PALIT.

DOJA, M. Q.—The quaternary ammonium iodides of dimethyl-*p*-toluidine 527

DOJA, M. Q. and A. MOKEET.—Preparation of *p*-diethylaminobenzaldehyde 542

DUNNICLIFF, H. B.—See M. A. HAMID.

DUTT, Sikhibhushan.—See Ram Nath MISRA, Radha Raman AGARWAL and Mahadeo Prasad GUPTA.

DUTT, Phanindra Nath.—See P. C. MITTER.

FARUQI, M. Z.—See D. N. CHATTERJI.

GANGULI, Kalipada.—See Promode Behari BHATTACHARYYA.

GANGULY, K. R.—See D. N. CHATTERJI.

GANGULY, S. N.—Studies on the addition of hydrogen halides to butadiene 580

GHOSE, T. P. and S. KRISHNA.—Constituents of the leaves of *Vitex negundo* 634

GHOSH, Amalendra Narayan.—See Priyadaranjan RAY.

PAGE

GHOSH, B. N.—The enzymes in snake-venom. Part I. Their action on hæmoglobin and on protein solutions of different p_H 450

GHOSH, B. N. and S. S. DE.—The enzymes in snake-venom. Part II. Their action on native proteins, on peptone and on the activity of trypsin 627

GHOSH, J. C. and B. B. RAY.—Oxidation of monochloroacetic acid by potassium permanganate at wave-lengths 366$\mu\mu$ and 436$\mu\mu$ with uranyl salt as photosensitiser 1

GHOSH, Nripendra Nath.—See P. C. RÂY.

GHOSH, Ranajit.—Synthesis in furan series. Part I. Synthesis of 2-ketotetrahydrofuran-4-acetic acid 323

GHOSH, Tejendra Nath.—Formation of heterocyclic compounds from thioacetylcarbamic acid derivatives. Part I. ... 86

GOSWAMI, M. and B. C. DAS-PURKAYASTHA.—Analytical uses of Nessler's reagent. A preliminary note 73

——Analytical uses of Nessler's reagent. Quantitative estimation of monosaccharides and disaccharides. Estimation of furfural. Part II. 315

GOSWAMI, M. and A. SHAHA.—Attempts to prepare ring glycerides. Preparation of tetrachlorodiglycerides of dicarboxylic acids 464

GUHA, Nirmal Chandra —See Prafulla Kumar BOSE.

GUHA, Sudhangsu Chandra.—See Anukul Chandra SIRCAR.

GUHA, Sisir Kumar.—Dyes derived from acenaphthene-quinone. Part V. 2-(6-Methyl)-thionaphthene-acenaphthylene-indigos ... 94

GUHA, Sisir Kumar and Hariprasad BASU-MALLICK.—Dyes derived from isatin. Azines and indigoid vat dyes ... 571

GUPTA, Jagannath.—Raman effect and molecular structure. Part I. The structure of the guanidinium ion 575

GUPTA, Mahadeo Prasad and Sikhibhushan DUTT.—The chemical examination of *Solanum xanthocarpum*, Schard and Wendle. Part I. The constituents of the oil from the seeds ... 613

HAMID, M. A., V. S. BHATIA and H. B. DUNNICLIFF.—The action of hydrogen sulphide on mercurous chromate ... 697

HIRWE, N. W.—See G. V. JADHAV.

ILAHI, Ijaz.—See Balwant SINGH.

PAGE

JADHAV, G. V. and S. N. RAO.—Derivatives of 1-hydroxy-2-naphthoic acid. Part II. 4-Halogeno-1-methoxy-2-naphthoic acids and their derivatives 645

JADHAV, G. V., S. N. RAO and N. W. HIRWE.—Derivatives of 1-hydroxy-2-naphthoic acid. Part I. 4-Halogeno-1-hydroxy-2-naphthoic acid and their derivatives 609

JOSHI, Shridhar Sarvottam and Sadashiv S. KULKARNI.—Studies in the coagulation of colloids Part XIV. Coagulation of colloid arsenious sulphide by mercuric chloride. Inadmissibility of viscosity and transparency as general criteria of coagulation 439

JOSHI, Shridhar Sarvottam and K. P. N. PANIKKAR.—Studies in the coagulation of colloids. Part XII Zonal effect in the change of refractivity during mutual coagulations ... 309

JOSHI, Shridhar Sarvottam and S. Jaya RAO —Studies in the coagulation of colloids. Part XI. Variation of optical refractivity during the coagulation of colloid manganese dioxide and new evidence for the discontinuity of the change ... 141

——Studies in the coagulation of colloids. Part XIII. Zonal effect in the opacity changes in the coagulation of colloid manganese dioxide 311

JOSHI, Shridhar Sarvottam and N. Hanumantha RAO.—Studies in the coagulation of colloids. Part XV New aspects of gold sol coagulation 755

JOSHI, Shridhar Sarvottam and P. V. Jagannatha RAO.—Thermo-ageing of colloids. Part I. Variation of refractivity ... 217

JUNG, Walter.—Immersion pyknometer 136

KANTAM, (Miss) P. LAKSHMI.—See B. B. DEY.

KOTWAL, R. D.—See A. N. MELDRUM.

KONDAIAH, K.—See M. B. RANE.

KATRAK, (Miss) B. N.—Preparation of compounds related to phenacetin 334

KAPUR, A. N.—See S. S. BHATNAGAR.

KAPUR, P. L.—See S. S. BHATNAGAR.

KRISHNA, S. and B. S. VARMA.—Active principles of *Myrsine africana*, Linn. 115

——See also T. P. GHOSE.

KULKARNI, Sadashiv S.—See Shridhar Sarvottam JOSHI.

PAGE

KUMARASWAMY, O. N. and B. L. MANJUNATH.—Chemical examination of the fixed oil from the seeds of *Celastrus paniculatus*, Willd. 353

LAL, Jagaraj Behari.—Constituents of the seeds of *Blepharis edulis*, Pers. Part I. 109
LAKHANI, M. P.—See Mata PRASAD.

MAITRA, S. R.—See N. M. BASU.
MAITRA, S. S.—See P. C. MITTER.
MANDAL, Kanailal.—See Panchanan NEOGI.
MANJUNATH, B. L.—See O. N. KUMARASWAMY.
MEHTA, P. R.—See R. C. SHAH.
MEHTA, S. M., M. U. PARMAR and Mata PRASAD.—The preparation of thorium phosphate gels 69
——Viscosity of thorium phosphate gel-forming mixtures during gelation 128
MELDRUM, A. N. and C. N. BAMJI.—6-Sulpho-*m*-cresotic acid and related compounds 641
MELDRUM, A. N. and R. D. KOTWAL.—A note on the constitution of the reduction product of trichloromethylparaconic acid 213
MELDRUM, Andrew Norman and Moreshwar Govind BHOJRAJ.—Condensation of chloral with acid amides. Properties of -CH (OH) CCl_3-group 185
MELDRUM, A.N. and G. M. Vad.—Constitution of the reduction product of chloral acetamide 117
——Condensation of chloral and bromal with polyhydric alcohols 118
MENON, E.V. and D. H. PEACOCK.—The stereochemistry of trivalent nitrogen compounds. Part I. The attempted resolution of some substituted derivatives of aniline 104
MISRA, Ram Nath and Sikhibhushan DUTT. - Dyes derived from acetylene dicarboxylic acid 98
MITRA, N. G.—See S. S. BHATNAGAR.
MITRA, Ramaprasad.—See Jnanendra Nath MUKHERJEE
MITTER, P. C. and Phanindra Nath Dutt.—Condensation of 3-and 4-nitrophthalic anhydrides with phenol and anisole ... 228
MITTER, P. C. and S. S. MAITRA,—Studies in the *iso*flavone series 236

PAGE

MITTER, P. C. and (Miss) Tanima SEN-GUPTA.—Studies in the anthraquinone series. Attempts to synthesise anthraquinone carboxylic acids of the morindone type ... 447

MOKEET, A.—See M. Q. DOJA.

MUKERJI, S. K.—See N. R. DHAR.

MUKHERJEE, Jnanendra Nath, Subodh Gobinda CHAUDHURY and Krishnadhan BHABAK.—Variation of the cataphoretic velocity of colloidal particles during aggregation ... 372

MUKHERJEE, Jnanendra Nath, Subodh Gobinda CHAUDHURY and Jyotirmoy SEN-GUPTA.—Variation of cataphorectic velocity of colloidal particles during aggregation. Part II. ... 428

MUKHERJEE, Jnanendra Nath, Ramprasad MITRA and Narayan Chandra SEN-GUPTA.—On the measurement of absolute rates of migration of ions by the method of moving boundaries. Part II. 42

MUKHERJEE, Sati Prasad.—See Kali Pada BASU.

NAIK, K. G. and S. A. VAISHNAV.—Interaction of sulphur dichloride with substances containing reactive methylene group. Part II. 25

——Interaction of thionyl chloride with substances containing the reactive methylene group. Part V 28

NARANG, Kartar Singh, Jnanendra Nath RÂY and Thakur Das SACHDEVA.—Quinoline derivatives. Part IV. 260

——See also Sant Singh BEDI.

NATH, Madhab Chandra.—See Kali Pada BASU.

NANDI, Sarajit Kumar.—See Panchanan NEOGI, also Satyaprasad ROYCHOUDHURY.

NEOGI, Panchanan and Kanai Lal MANDAL.—Experiments on resolution of co-ordinated inorganic compounds into optical isomers. Co-ordinated cadmium compounds with racemic and active propylenediamine 224

NEOGI Panchanan and Sarajit Kumar NANDI.—New compounds of gallium. Part I. 399

NEVGI, M. B.—See S. S. BHATNAGAR.

PALIT, C. C. and N. R. DHAR.—Oxidation of glucose in presence of insulin, glutathione and other substances and the probable mechanism of biological oxidations ... 502

PAGE

PANIKKAR, K. P. N.—See Shridhar Sarvottam JOSHI.
PARMAR, M. U.—See S. M. MEHTA.
PAUL, Prafulla Kumar.—On phthalide formation ... 599
PEACOCK, D. H.—See E. V. MENON.
PRASAD, Mata and Jagdish SHANKER—An *X*-ray investigation of the crystals of benzoin 123
——*X*-ray investigation of the crystals of *o*-nitrodiphenylamine 663
PRASAD, Mata, M. P. Lakhani and Jagdish SHANKAR.—An *X*-ray investigation of the crystals of *m*-nitrodiphenyl ... 519
——See also S. M. MEHTA.
PURI, M. L.—See S. S. BHATNAGAR.

RAKSHIT, P. C.—See S. C. DE.
RANE, M. B., K. KONDAIAH and M. K. RATNAM.—Removal of antimony from its solutions by nitric acid ... 544
RANGANATHAN, S. K.—A synthesis of *cis*- and *trans*-*dl*-1-*iso*propyl*cyclo*propane-1:2-dicarboxylic acid and experiments towards the resolution of the *cis*-*dl*-acid 419
RAO, N. Hanumantha.—See Shridhar Sarvottam JOSHI.
RAO, P. V. Jagannatha.—See Shridhar Sarvottam JOSHI.
RAO, S. Jaya.—See Shridhar Sarvottam JOSHI.
RAO, S. N.—See G. V. JADHAV.
RATNAM, M. K.—See M. B. RANE.
RAY, B. B.—See J. C. GHOSH.
RAY, Anil Chandra.—See P. C. RÂY ; also Prafulla Kumar BOSE.
RÂY, JNANENDRA Nath.—See Kartar Singh NARANG, also Narindra Nath CHOPRA.
RÂY, Prafulla Chandra and Nripendra Nath GHOSH.—Complex compounds of iridium. Part IV. 138
RÂY, P. C. and Anil Chandra RAY—On the fluorination of organic compounds. Part II. 427
RÂY, Priyadaranjan and Amalendra Narayan GHOSH.—Complex metalammonium selenites and selenito-metalammines ... 494
RAY, Susil Kumar.—Parachor and chemical constitution. Part V. The structure of liquid crystals 194
——Parachor and structure of formic acid ... 484
RAY, Susil Kumar and Rama Ranjan BHATTACHARYA.—On the study of polyhalides. Part IV. Formation and dissociation of polyhalides of ammonium and substituted ammonium bases 456

PAGE

RENGACHARI, S.—See B. B. DEY.
ROY, Anil Chandra.—See Prafulla Kumar BOSE.
ROY, G. C.—See K. M. SIL.
ROY, Sachindra Nath.—A method for the estimation of lead volumetrically by Fajan's method 40
——A note on the use of adsorption indicators in acidimetry and alkalimetry 486
ROYCHOUDHURY, Satyaprasad, Sarajit Kumar Nandi and Jiban Krishna BANERJEE.—On activated charcoal. Part II Purification by washing with water and by activation ... 410
RUDRA, Mahendra Nath.—Studies in vitamin C. Part II. The vitamin C contents of the liver and muscle of some Indian fresh-water fish 740

SACHDEVA, Thakur Das.—See Kartar Singh NARANG.
SAHA, Srish Kumar.—A modified micro method for the estimation of nitrogen in soil 72
SARKAR, Pulin Bihari.—Electronic theory of valency and the constitution of aromatic diazo compounds ... 19
SEN, Dines Chandra.—Studies on cyclic thioketones. Part I Synthesis of non-polymerised thio*cyclo*hexanone, thio*cyclo*pentanone and their derivatives 268
——Studies in the camphor series. Part III.—Tautomeric behaviour of thiocamphor and the activity of its sodium derivative 523
SEN, Sailes Chandra.—See Anukul Chandra SIRCAR.
SEN-GUPTA, Jyotirmoy.—See Jnanedra Nath MUKHERJEE, also Subodh Gobinda CHAUDHURY.
SEN-GUPTA, Narayan Chandra.—See Jnanendra Nath MUKHERJEE.
SEN-GUPTA, (Miss) Tanima.—See P. C. MITTER.
SHAH, Narshinh Muljibhai and Rupchand Lilaram ALIMCHANDANI.—Chloral derivatives of salicylic acid ... 475
SHAH, R. C. and P. R. MEHTA.—*C*-Alkylresorcinols. Part II. Synthesis of polyalkyl derivatives 358
——A new and convenient synthesis of 2:4-′ dihydroxybenzophenone 368
SHAHA, A.—See M. GOSWAMI.
SHANKARANARAYAN, S.—See Phuldeo Sahay VARMA.
SHANKER, Jagdish.—See Mata PRASAD.

PAGE

SHARMA, R. K.—Application of the thiocyanogen value in the quantitative determination of oleic and linolic acids in natural oils, which are free from linolenic acid, according to Kauffman 151

SHARMA, R. L.—See S. S. BHATNAGAR.

SIL, K. M., G. C. ROY and P. N. DAS-GUPTA.—A new method for the separation of lead from copper and their subsequent estimations 747

SINGH, Balwant and Ijaz ILAHI.—Potentiometric studies in oxidation-reduction reactions. Part I. Oxidation with potassium oxalate 717

SINGH, Mahan.—The rotatory powers of substituted camphoranilic acids 467

SINGH, Mahan and Manohar SINGH.—Studies on optical activity and chemical constitution. Part III. Optically active acids and bases 743

SINGH, Manohar.—See Mahan SINGH.

SIRCAR, Anukul Chandra and Sudhangsu Chandra GUHA.—Condensations of furil and furoin 704

SIRCAR, Anukul Chandra and Dwipendra Chandra CHOWDHURY.—Studies in acenaphthenequinone series. Part III. ... 709

SIRCAR, Anukul Chandra and Saliesh Chandra SEN.—Studies in the acenaphthenequinone series. Part II. ... 482

SITHARAMAN, M. V.—See B. B. DEY.

SREENIVASAMURTHYACHAR, C.—See Phuldeo Sahay VARMA.

SRIKANTAN, B. S.—Behaviour of gases under the influence of high frequency discharge. Ammonia and hydrogen ... 79

SRINIVASAN, M. K.—See Phuldeo Sahay VARMA.

SRINIVASAN, T. K.—See B. B. DEY.

SUBRAHMANIAN, T. S.—See Phuldeo Sahay VARMA.

SUNAWALA, S. D.—A note on the estimation of formic acid in commercial acetate of lime 545

TANDON, S. P.—See N. R. DHAR.

VAD, G. M.—See A. N. MELDRUM.

VAISHNAV, S. A.—See K. G. NAIK.

VARADANAM, Ch. I.—See N. R. DHAR.

VARMA, B. S.—See S. KRISHNA.

PAGE

VARMA, Phuldeo Sahay and S. SHANKARANARAYANAN.—Halogenation. Part XIII. Bromination and iodination of some halogenated benzenes 31
VARMA, Phuldeo Sahay and C. SREENIVASAMURTHYACHAR.—Halogenation. Part XIV. Iodination of aromatic hydrocarbons and bromo toluenes 187
VARMA, Phuldeo Sahay and M. K. SRINIVASAN.—Halogenation. Part XV. Chlorination and bromination of cumene and *p*-cymene 189

VARMA, Phuldeo Sahay and T. S. SUBRAHMANIAN.—Halogenation. Part XVI. Bromination and iodination of mesitylene ... 192
WALAWALKER, D. G.—A note on solid sugars from mohuwa flower syrup 657
WALI, M. A.—See R. D. DESAI.

Journal of the Indian Chemical Society
Vol. XIII, 1936.

SUBJECT INDEX

A

PAGE

Acenaphthenequinone, dyes derived from (Ghosh) 94
  action of sodium acetate and acetic anhydride on (Sircar and Chowdhury) 714
  action of alcoholic potash on (Sircar and Chowdhury) 714
  condensation of glycollic acid with (Sircar and Chowdhury) 715
Acenaphthylene-2-(6-methyl)-thionaphthene- indigos (Guha) ... 94
Acetamide, β-dichlorovinyl-, chloralphenyl-, β-dichlorovinylphenyl-, (Meldrum and Bhojraj) ... 186
Acetoacetanilide, interaction of sulphur dichloride with (Naik and Vaishnav) 26
Acetoacet-α-(β-)-naphthylamide, interaction of sulphur dichloride with (Naik and Vaishnav) 27
Acetoacet-*o*-(*p*-) toluidide, interaction of sulphur dichloride with (Naik and Vaishnav) 27
Acetoacet-xylidide (1:3:4-or 1:4:5-), interaction of sulphur dichloride with (Naik and Vaishnav) 27
Acetophenone, 5-ethyl-6-methyl-2:4-dihydroxy-, and derivatives (Shah and Mehta) 365
Acetylene dicarboxylic acid, dyes derived from (Misra and Dutt) 98
Acetylenein, phenol-, resorcinol-, tetrabromoresorcinol-, phloroglucinol-, orcinol-, *m*-dimethylamidophenol-, *m*-diethylamidophenol-, *m*-phenylenediamine-(Misra and Dutt)... 100-102
Adsorption indicators, the use of (Roy) 486
C-Alkyl resorcinols (Shah and Mehta) 358
Alumina, the physico-chemical properties of electrodialysed gels of (Bhattacharyya and Ganguli) 204, 205, 547
Amarbelin and derivatives (Agarwal) 534

PAGE

Amarbelitin (Agarwal) 535

Aminoguanidine, derivatives of (De and Rakshit) ... 513-518

Ammonia and hydrogen, their behaviour under the influence of high frequency discharge (Srikantan) 79

Anhydrodichloral glycol (Meldrum and Vad) 118

Anthraquinone, 1:8-, 1:7-, 2:6-, and 2:7-dihydroxy- (Mitter and Dutt) 231-235

Anthraquinone carboxylic acids of the morindone type, attempts to synthesise (Mitter and Sen-Gupta) 447

Antimony, removal of, from its solutions by nitric acid (Rane, Kondaiah and Ratnam) 544

Aromatic diazo compounds, the constitution of (Sarkar) ... 19

Arsenic, estimation of small quantities of, in medico-legal cases (Chatterji, Ganguly and Faruqui) 751

Arsenious sulphide colloid, coagulation of, by mercuric chloride (Joshi and Kulkarni) 439

Atophan, some synthetic compounds related to (Bose and Guha) 700

Ayapanin, isolation and constitution of (Bose and Roy) ... 586

Azlactone of β-resorcylaldehyde-dimethylether (Mitter and Maitra) 238

B

Benzaldehyde, 3:5-diethyl-2:6-dihydroxy-, 2-methyl-3-ethyl-4:6-dihydroxy-, 3:5-diethyl-4-methyl-2:6-dihydroxy- (Shah and Mehta) 361-366

Benzamide, 6-acetylamino-3:4-methylenedioxy- (Bedi and Narang) 254

  β-Dichlorovinyl- (Meldrum and Bhojraj) ... 186

  condensation with resorcinol (Shah and Mehta ... 370

Benzanilide, condensation with resorcinol (Shah and Mehta) ... 369

Benzimidazole, 2-dicarbethoxymethyl-, 2-methyl-, 2-diacetylmethyl- (Ghosh) 92

2:3-Benzofuro- (12 or 11 or 10-methyl)-11-hydroxy-, quinoline-4-carboxylic acid (Bose and Guha) 702-703

Benzoic acid, 5:6-dimethoxy-2 (2'-hydroxy-3'-carboxy-5'-bromo-benzyl)- (Mitter and Sen-Gupta) 449

  condensation with resorcinol (Shah and Mehta) ... 370

Benzophenone (2:4-dihydroxy-), synthesis of (Shah and Mehta) 368

PAGE

Benzopyranol anhydrochloride, 2-phenyl-4-keto-1:2:3:4-tetrahydro- (Desai and Wali) 737

Benzopyrylium chloride, 6:8-diethyl-5-hydroxy-5′:6′-dimethoxy-2:3 (3′:2′)-indeno-, 5-methyl-6-ethyl-7-hydroxy-5′:6′-dimethoxy-2:3 (3′:2′)-indeno-, 6:8-diethyl-7-methyl-5-hydroxy-5′:6′-dimethoxy-2:3(3′:2′)-indeno- (Shah and Mehta)... 361-367

2-Benzoyl (2′-hydroxy or 4′-methoxy)- benzoic acid, 3-nitro or amino or hydroxy-, 6-nitro or amino-, 4-nitro or amino or hydroxy-, 5-nitro or amino or hydroxy, and derivatives (Mitter and Dutt) 231-235

Biological oxidations, the probable mechanism of (Palit and Dhar) 502

Blepharis edulis, constituents of the seeds of (Lal) 109

Bromal, condensation with polyhydric alcohols (Meldrum and Vad) 118

4-Bromo-2-aceto-1-naphthol and derivatives (Chakravarti and Bagchi) 695

4-Bromo (chloro-) -1-hydroxy-2-naphthoic acid, derivatives of (Jadhav, Rao and Hirwe) 611-612

4-Bromo (chloro-)-1-naphthol, synthesis of coumarins and chromones from (Chakravarti and Bagchi) 649

Bromotoluenes, iodination of (Varma and Sreenivasamurthyachar) 187

Butadiene, the addition of hydrogen halides to (Ganguly) ... 580

Butane-δδ-dichloro-αβ-dicarboxylic acid and derivatives (Meldrum and Kotwal) 214

*iso*Butyramide, chloral-, β-dichlorovinyl-(Meldrum and Bhojraj) 186

C

Cadalene, a new synthesis of (Chatterjee) 588

Cadmium compounds, (co-ordinated) with racemic and active propylenediamine (Neogi and Mandal) 224

Cadmium tripropylenediamine chloride, bromide, iodide, thiocyanate, camphor nitronate, camphor sulphonate, bromocamphor sulphonate, tartrate (Neogi and Mandal) ... 224-226

Cadmium, (*l* and *d*-) tripropylenediamine chloride, bromide, iodide (Neogi and Mandal) 226-227

Calotropis gigantea, proteinase in the milky juice of (Basu and Nath) 34

PAGE

purification and activation of (BASU and NATH) ... 35-37

Camphoranilic acid, 4′- (or 3′ or 4′) dimethylamino-, (SINGH and SINGH) 745

Camphoranilic acid, *o*-ethyl-, *p*-ethyl-, *m*-aceto-, *p*-aceto-, *m*-nitro-, *p*-nitro-, *m* (*p*)-amino-, *m*-(*p*-) acetylamino-, *m*(*p*-)-fluoro-, 2′-nitro-4′-ethyl-, 2′-nitro-3′-fluoro-, 2′-nitro-4′-fluoro-, 2′-nitro-4′-aceto- (SINGH) 471-72

Camphoranilic acids (substituted), the rotatory powers of (SINGH) 467

Camphoric anhydride, condensation with monosubstituted amines (SINGH)... 470
  condensation with aminodimethylanilines (SINGH and SINGH) 745

Camphoro-*o*-dimethylaminophenylimide (SINGH and SINGH) ... 745

Camphorophenylimide, *o*-ethyl-, *p*-ethyl- (SINGH) 472

n-Capronamide, chloral-, *β*-dichlorovinyl-(MELDRUM and BHOJRAJ) 186

n-Caprylamide, chloral-, *β*-dichlorovinyl- (MELDRUM and BHOJRAJ) 186

1-Carboxy*cyclo*hexane (4-methyl-)-1-*α*-glutaric acid and triethyl ester (CHATTERJEE) 539, 590

Cataphoretic velocity of colloidal particles during aggregation, variation of (MUKHERJEE, CHAUDHURY and SEN-GUPTA) ... 428
  (MUKHERJEE, CHAUDHURY and BHABAK) ... 372

Celastrus paniculatus, Willd., chemical examination of the fixed oil from the seeds of (KUMARASWAMY and MANJUNATH) ... 353

Cellulose, measurement of molecular areas of, by surface tension method (CHOWDHURY and BARDHAN) 294

Cellulose, molecular size of, from different sources (CHOWDHURY and BARDHAN) 240
  molecular weights of (CHOWDHURY and BARDHAN... 245
  molecular weight of, in viscose solution (CHOWDHURY and BARDHAN) 249
  (degraded) molecular weight of (CHOWDHURY and BARDHAN) 251

Charcoal (activated), purification by washing with water and by activation (ROYCHOUDHURY, NANDI and BANERJEE) 410
  effect of electrolytes on surface charge of (ROYCHOWDHURY, NANDI and BANERJEE) 416
  coated with various substances, properties of (ACHARYA) 723

PAGE

Chloral acetamide, constitution of the reduction product of (MELDRUM and VAD) 117
Chloral, condensation with acid amides (MELDRUM and BHOJRAJ) 185
condensation with polyhydric alcohols (MELDRUM and VAD) 118
Chlorates, estimation of (BANERJEE) 301
4-Chloro-2-aceto-1-naphthol and derivatives (CHAKRAVARTI and BAGCHI) 692
chalkones from (CHAKRAVARTI and BAGCHI) 696
4-Chloro-1-naphthol, preparation of (CHAKRAVARTI and BAGCHI) 651
4-Chloro-2-propio-1-naphthol and derivatives (CHAKRAVARTI and BAGCHI) 694
β-Chlorovinylmethylarsenious oxide and sulphide (DAS-GUPTA) 307
β-Chlorovinylmethylarsinic acid (DAS-GUPTA) 307
β-Chlorovinylmethylchloroarsine (DAS-GUPTA) 306
β-Chlorovinylmethylphenylarsine (DAS-GUPTA) 308
Chow chow, experiments with (DEY, RENGACHARI and SITHARAMAN) 395, 396
Chromone, 6-chloro-2:8-dimethyl-, 6-chloro-2:3:8-trimethyl-, 6-chloro-2 : 8- dimethyl-3-ethyl-, 6- chloro-2 : 8-dimethyl-3-propyl-, 8-chloro-2 : 3 : 6-trimethyl-, 8-chloro-2 : 6-dimethyl-3-ethyl-, 6-chloro-2 : 3 : 7-trimethyl-, 6-chloro-3-ethyl-2 : 7-dimethyl-, 6-chloro-3-propyl-2 : 7-dimethyl-, 6-nitro-2 : 3 : 8-trimethyl-, 6-nitro-2 : 8-dimethyl-3-ethyl-, 6-nitro-2 : 8-dimethyl-3-propyl-, 8-nitro-2 : 7-dimethyl-, 8-nitro-2:7-dimethyl-3-ethyl- (CHAKRAVARTI and BANERJEE) ... 623-626
Coagulation, (mutual) zonal effect in the change of refractivity during (JOSH and PANIKKAR) 309
of colloid manganese dioxide, zonal effect in the opacity changes in the (JOSHI and PANIKKAR) ... 311
Cobaltammines, influence of dilution on the molecular refractivities of (BHATTACHARYA) 284
Cobalt chloride, colour changes in, a magnetic study of (BHATNAGAR, KAPUR and KAPUR) 489
Cod liver oil emulsions, investigations on (CHATTERJEE) ... 563

PAGE

Colloidal particles, cataphoretic velocity of, variation during aggregation (MUKHERJEE, CHAUDHURY and BHABAK)... 372
(MUKHERJEE, CHAUDHURY and SEN-GUPTA) ... 428
Colloids, thermo-ageing of (JOSHI and RAO) 217
variation of refractivity of (JOSHI and RAO) ... 217
Complex cyanides, influence of dilution on the molecular refractivities of (BHATTACHARYA) 284
Co-ordinated inorganic compounds, resolution of, into optical isomers (NEOGI and MANDAL) 224
Copper, separation of, from lead, a new method of (SIL, ROY and DAS-GUPTA) 747
Cotarnomethyl carbonyl chloride, 5-bromo- and derivatives (DEY and KANTAM) 282
Catarnomethyl carboxylic acid and derivatives (DEY and KANTAM) 282
Cotarnine, condensation of, with phosgene (DEY and KANTAM) ... 281
action of sulphuric acid on (DEY and SRINIVASAN) ... 337
Coumaranones, condensation of, with isatic acid (BOSE and GUHA) 703
Coumarin, 5-methyl-6-ethyl-7-hydroxy-, 4 : 7-dimethyl-6-ethyl-5-hydroxy-, 6 : 8-diethyl-7-methyl-5-hydroxy-, 6 : 8-diethyl-4 : 7-dimethyl-5-hydroxy- (SHAH and MEHTA) ... 361-367
Coumarin, 8-chloro-4 : 6-dimethyl-, 8-chloro-3 : 4 : 6-trimethyl-, 8-chloro-4 : 6-dimethyl-3-ethyl-, 3 : 8-dichloro-4 : 6-dimethyl-, 6-chloro-3 : 4 : 7-trimethyl-, 6-chloro-3-ethyl-4 : 7-dimethyl-, 3:6-dichloro-4 : 7-dimethyl- (CHAKRAVARTI and BANERJEE) 623-625
Coumarin (6-chloro-7-methyl-)-4-acetic acid (CHAKRAVARTI and BANERJEE) 625
Coumarin (6-chloro-4 : 7-dimethyl)-3-acetic ester (CHAKRAVARTI and BANERJEE) 625
Coumarin- (6 : 8-diethyl-5-hydroxy-, 5-methyl-6-ethyl-7-hydroxy-, 6 : 8-diethyl-7-methyl-5-hydroxy-)-3-carboxylic acids, ethyl esters of (SHAH and MEHTA) 361-367
Cresols (halogenated and nitro-), synthesis of coumarins and chromones from (CHAKRAVARTI and BANERJEE) 619
m-Cresotic acid (6-sulpho-) and related compounds (MELDRUM and BAMJI) 641
m-Cresotic acid, 2-bromo-6-sulpho-, 2-bromo-, 2 : 6-dinitro-, 2-nitro 6-sulpho- (MELDRUM and BAMJI) ... 642-644
Cumene, chlorination of (VARMA and SRINIVASAN) 189

PAGE

Cuscuta reflexa, chemical examination of (AGARWAL and DUTT) 264
 (AGARWAL) 531
p-Cymene, chlorination and bromination of (VARMA and SRINIVASAN) 189

D

Denitrification in sunlight and its retardation (DHAR and MUKERJI) 555
Desoxyfuroin, phenylcyanoethylene-, benzoylaminocarboxyethylene-, cyanocarbethoxyethylene-, acetylcarbethoxyethylene, dicarbethoxyethylene-, diacetylethylene (SIRCAR and GUHA) 706-707
Diamagnetic susceptibilities of tin, in di and tetra valency states (BHATNAGAR, NEVGI and SHARMA) ... 273
 influence of temperature on (BHATNAGAR, NEVGI and SHARMA) 279
 in the dissolved state (BHATNAGAR, NEVGI and SHARMA) 279
Diazo compounds, constitution of (SARKAR) 19
αα-Dichlorohydrin, reaction product with phthalic anhydride (GOSWAMI and SHAHA) 466
β-Dichlorovinylmethylarsine (DAS-GUPTA) 308
β-Diethylaminobenzaldehyde, preparation of (DOJA and MOKEET) 542
Diethylanil-alloxan (DOJA and MOKEET) 543
Diethyl 1-cyano*cyclo*hexane (4-methyl-)- 1-α-cyanoglutarate (CHATTERJEE) 539, 590
4 : 5-Difuryl-2-iminazolone (SIRCAR and GUHA) 707
2′: 3′-Difurylindole (SIRCAR and GUHA) 708
2′: 3′-Difuryl-(α-or-β-)-naphthindole (SIRCAR and GUHA) ... 708
4 : 5-Difurylthioiminazolone (SIRCAR and GUHA) 708
2′: 3′-Difuryl-(*o*- or *p*)-toluindole (SIRCAR and GUHA) ... 708
Dihydroiminazole, 2-dicarbethoxymethyl- (GHOSH) ... 93
Dihydroresorcinols (DESAI and WALI) 735
Dihydro-1:2:4- triazole (3-keto-2-phenyl-)-5-acetic acid (GHOSH) . 90
Dihydro-1 : 2 :4-triazole, 3-keto-2-phenyl 5-dicarbethoxymethyl-, 2-phenyl-3-keto-5-methyl-, 3-keto-5-diacetyl-methyl-, 3-keto-5-acetylmethyl- (GHOSH)... 90-91
β-Diketones, action of aminoguanidines on (DE and RAKSHIT) 513-518

PAGE

2′:4′-Dimethoxyphenyl-2 : 4 : 6-trihydroxyacetophenone (MITTER and MAITRA) 238
m-Dimethylaminophenylbenzylamine, *p*-toluenesulphonyl (MENON and PEACOCK) 106
Dimethyldihydroresorcinol, furfural-bis-, *p*-dimethylaminobenzal-bis-, and derivatives (DESAI and WALI) 739
Dimethyl-*p*-toluidine, the quaternary ammonium iodides of (DOJA) 527
Diphenyl acetates, synthesis of (CHATTERJEE) 593
Diphenyl (4 or 6 or 5-methyl-)-2-acetic acid, ethyl esters of (CHATTERJEE) 597
Disaccharides, quantitative estimation of (GOSWAMI and DAS-PURKAYASTHA) 315

E

Electrokinetic potential and peptisatson, on the relation between (CHAUDHURY and SEN-GUPTA) 670
Enzymes in snake-venom, action on native proteins, peptone and on the activity of trypsin (GHOSH and DE) ... 627-631
on hemoglobin and protein solutions of different p_H (GHOSH) 450
Ethane, *s*-di -β-tribromo-α-hydroxyethoxy- (MELDRUM and VAD) 120
Ethylacetamide, β-trichloro-α-chloro-, β-trichloro-α-anilino- (MELDRUM and VAD) 117-118
Ethylbenzylaniline sulphonic acid, brucine salt of (MENON and PEACOCK) 105
Ethyl α-*iso*propylacrylate, condensation with ethyl diazoacetate (RANGANATHAN) 422
Ethyl 5-*iso*propyl-Δ′-pyrazoline-3:5-dicarboxylate (RANGANATHAN) 422
Ethylideneglycol, β-trichloro-, β-tribromo- and ββ-dichloro- (MELDRUM and VAD) 119,120
Ethyl methoxyethylidene mono (di-) malonate (GHOSH) ... 326

F

Ferric hydroxide sol (negative), a modified method of preparation of (DAS and DE) 197
comparative stabilisation of (DAS and DE) ... 201

PAGE

Ferric hydroxide, physico-chemical properties of electrodialysed gels of (BHATTACHARYA and GANGULI) 204, 205, 547
*iso*Flavone, 5 : 7-dihydroxy-2′: 4′-dimethoxy-2-methyl-, and diacetyl derivative (MITTER and MAITRA) 239
Fluorination of organic compounds (RÂY and RAY) ... 427
Formic acid, structure of and the parachor (RAY) 484
Furan-4-acetic acid, 2-ketotetrahydro- (GHOSH) 322
Furfural, estimation of (GOSWAMI and DAS-PURKAYSTHA) ... 315
Furfurane, 3-acetoxy-2-phenyl-4 : 5-acenaphthylene- (SIRCAR and CHOWDHURY) 714
Furil, condensation of, with salicylaldehyde and furfuraldehyde (SIRCAR and GUHA) 704, 706
Furil, dithioureine and diureine (SIRCAR and GUHA)... ... 707
Furiliminazole, 4′(3′)-hydroxy-2-phenyl-, 4′-nitro-2-phenyl-(SIRCAR and GUHA) ... ... - ... 705
Furoin, condensation of (SIRCAR and GUHA) 704

G

Gallium, new compounds of (NEOGI and NANDI) 399
Gallium hydroxides, *d*- (*l*, *r* and *meso*)- tartrates, basic acetate, formate, oxalate (*n*) citrate, lactate, malate, phosphates (acid and normal), hypophosphite (acid and normal) (NEOGI and NANDI) 400-403
Gels, saturated with different cations, moisture retention capacity of (BHATTACHARYA and GANGULY) 547
Gel, thorium phosphate, viscosity of, during gelation (MEHTA, PARMAR and PRASAD) 128
preparation of (MEHTA, PARMAR and PRASAD) ... 69
Glucose, oxidation of, in presence of insulin and glutathione (PALIT and DHAR) 502
Glutaric acid (β-methoxymethyl), anhydride and ethyl ester (GHOSH) — 327
Glycerol $\alpha\beta$-(β'-tribromoethylidene)- (MELDRUM and VAD) ... 121
Guanidinium ion, the structure of (GUPTA) 575

H

Halogenated benzenes, bromination and iodination of (VARMA and SHANKARANARAYANAN) 31

PAGE

Halogenation, (Varma and Shankaranarayanan) ... 31
Halogenation (Varma and Sreenivasmurthyachar) ... 187
(Varma and Srinivasan) 189
(Varma and Subrahmanian) 192
4-Halogeno-1-hydroxy-2-naphthoic acid and derivatives (Jadhav, Rao and Hirwe) 609
4-Halogeno-1-methoxy-2-naphthoic acids and derivatives (Jadhav and Rao) 645
Hexahydrodiphenyl (1-hydroxy-4 or 5 or 6 -methyl-) 2-acetic acid-2-carboxylic acid, lactones of the ethyl esters of (Chatterjee) 598
Hexahydrodiphenyl (1-hydroxy-4 or 5 or 6- methyl-)-2-acetic acid, ethyl esters of (Chatterjee) 597
Hexahydrodiphenyl-2-acetic acid and ethyl ester (Chatterjee) ... 597
*cyclo*Hexane (4-methyl-) spiro-*cyclo*pentane and derivatives (Chatterjee) 540-551, 591-592
*cyclo*Hexane, 1-phenyl-4-(α-hydroxy-βββ-trichloroethyl)-, 1:1-dimethyl-4- (α-hydroxy-βββ-trichloroethyl)-3:5-dione (Desai and Wali) 738-739
*cyclo*Hexane-spiro*cyclo*pentane, synthesis of (Chatterjee) ... 536
cyclo-Hexanone (4 or 5 or 6-methyl) -2-carboxylic acid -2-acetic acid, diethyl esters of (Chatterjee) 595
*cyclo*Hexanone (4 or 5 or 6-methyl) -2-acetic acid and ethyl esters (Chatterjee) 596
Highly concentrated sols, preparation and properties of (Dhar and Varadanam) 602
Horse radish, experiments with (Dey, Rengachari and Sitharaman) 394, 395
Hydrocarbons (aromatic), iodination of (Varma and Sreenivasmurthyachar) 187
Hydrogen and ammonia, their behaviour under the influence of high frequency discharge (Srikantan) 79
1-Hydroxy-2-naphthoic acid, derivatives of (Jadhav and Rao) ... 645
(Jadhav Rao and Hirwe) 609

I

Iminazole, *N*-benzylacenaphthylene- ψ- phenyl-, *N*-methylacenaphthylene-, *N*-ethylacenaphthylene-ψ-methyl- (Sircar and Chowdhury) 713

PAGE

Indazine, acenaphtheno-, acenaphtheno-5-nitro-, acenaphtheno-5 : 7-dinitro-(GUHA and BASU-MALLICK) ... 572-573

Indian fresh-water fish, the vitamin C contents of the liver and muscle of (RUDRA) 740

Indigo, 2:3-naphthathiophene-3′-(5′-iodo)-indole, 2:3-naphthathiophene-3′-(5′-bromo-7′-nitro-)-indole, 2:3-naphthathiophene-3′-(5′:7′-dinitro)-indole-(GUHA and BASU-MALLICK) 573-574

Indigoid vat dyes (GUHA and BASU-MALLICK) 571

Iridium, complex compounds of (RÂY and GHOSH) ... 138

Isatic acid, condensation of, with coumaranones (BOSE and GUHA) 702

Isatin, dyes derived from (GUHA and BASU-MALLICK) ... 571

K

β-Ketonic esters, action of aminoguanidines on (DE and RAKSHIT) 509

Kostanecki's reaction, on the limited applicability of (CHAKRAVARTI and BAGCHI) 689

L

Lead, estimation of (ROY) 40

a method for separation of, from copper, (SIL, RAY, and DAS-GUPTA) 747

Liquid crystals, the structure of (RAY) 194

M

Magnetic susceptibility of the -CH_2 group, a critical examination of Pascal's value for (BHATNAGAR and MITRA) ... 329

Malon di-α-naphthylamide, interaction of, with thionyl chloride (NAIK and VAISHNAV) 30

Malon di-o-(p-or m-) tolylamide, interaction of, with thionyl chloride (NAIK and VAISHNAV) 30

Malondiphenylamide, interaction of, with thionyl chloride (NAIK and VAISHNAV) 30

Malondixylidide (1 : 3 : 4 or 1 : 4 : 5) (NAIK and VAISHNAV) ... 30

Manganese dioxide (colloid), variation of optical refractivity during the coagulation of (JOSHI and PANIKKAR) ... 141

PAGE

Mesitylene, bromination and iodination of (VARMA and SUBRAHMANIAN) 192
Mesitylene, 2-bromo-4-iodo- (VARMA and SUBRAHMANIAN) ... 193
4-Methoxy-5-carboxy-1-α-hydroxy-βββ-trichloroethylbenzene and derivatives (SHAH and ALIMCHANDANI) 476
Methoxy-oxypalmatine (CHOPRA and RÂY) 478
Methylbornylene sulphide (SEN) 525
4-Methyl*cyclo*hexanone, transformation in spiro compound from, (CHATTERJEE) 588
Methylene bis-phenol-betaine of 2-methyl-6:7-dihydroxy-8-methoxy-3:4-dihydro*iso*quinolinium hydroxide and derivatives (DEY and SRINIVASAN) 341
Migration of ions, on the absolute rates of, by the method of moving boundaries (MUKHERJEE, MITRA and SEN-GUPTA) ... 42
Milk dehydrogenase, action of dyestuffs and other substances on (BASU and MUKHERJEE) 11
Mohuwa flower syrup, solid sugars from (WALAWALKAR) ... 657
Molecular structure and Raman effect (GUPTA) 575
Monochloroacetic acid, oxidation of, by potassium permanganate with uranyl salt as photosensitiser (GHOSH and RAY) ... 1
Monosaccharides, quantitative estimation of (GOSWAMI and DAS-PURKAYASTHA) 315
Moving boundaries, the measurement of the absolute rates of migration of ions by the method of (MUKHERJEE, MITRA and SEN-GUPTA) 42
Myrsine africana, Lin., active principle of (KRISHNA and VARMA) 115
Myristicinic acid, phthalide from (PAUL) 601

N

α-Naphtha-*o*-coumaric acid, 7-chloro- (CHAKRAVARTI and BAGCHI) 652
1:2-αβ-Naphthapyrone (6-chloro-) -4-acetic acid (CHAKRAVARTI and BAGCHI) 655
1:2-αβ-Naphthapyrone, (6-chloro-4-methyl-)-3-acetic ester CHAKRAVARTI and BAGCHI) 655
1:2-αβ-Naphthapyrone, 6-chloro-, 6-chloro-4-methyl-, 6-chloro-3:4-dimethyl-, 6-chloro-4-methyl-3-ethyl-, 6-chloro-4-methyl-3-propyl-, 6-chloro-4-methyl-3-*iso*butyl-, 6-chloro-4-methyl-3-benzyl-, 3:6-dichloro-4-methyl-, 6-chloro-4-phenyl-, 6-chloro-

PAGE

4-methyl-3-phenyl-, 6-bromo-4-methyl-, 6-bromo-3:4-dimethyl-, 6-bromo-4-methyl-3-benzyl (CHAKRAVARTI and BAGCHI) 654-656

1:2-αβ-Naphthapyrone, 6-chloro-3:4-dimethyl-, 6-chloro-4-methyl-3-phenyl-, 6-chloro-3-methyl-4-ethyl (CHAKRAVARTI and BAGCHI) 693-695

1:4-αβ-Naphthapyrone, 6-chloro-2-methyl-3-acetyl-, 6-chloro-2-phenyl-3-benzoyl-, 6-chloro-, 6-chloro-2:3-dimethyl CHAKRAVARTI and BAGCHI) 692-695

1:4-αβ-Naphthapyrone, 6-chloro-2:3-dimethyl-, 6-chloro-2-methyl-3-ethyl-, 6-chloro-2-methyl-3-propyl-, 6-chloro-2-methyl-3-*iso*butyl-, 6-bromo-2:3-dimethyl- and styryl derivatives (CHAKRAVARTI and BAGCHI) 654-656

2-α (or β)-Naphthylquinoline-4-carboxylic acid (BOSE and GUHA) 703

Nessler's reagent, analytical uses of (GOSWAMI and DAS-PURKAYASTHA) 73, 315

Nitrates, estimation of (BANERJEE) 302

Nitrites to nitrates, oxidation of, in sunlight (DHAR and TANDON) 180

m-(or *p*-) Nitroaniline, *p*-toluene-sulphonylbenzyl-(MENON and PEACOCK) 105, 107

p-Nitrodiphenyl, investigation of the crystals of (PRASAD, LAKHANI and SHANKER) 519

Nitrogen, available, in tropical soils (DHAR and MUKHERJI) ... 23

Nitrogen fixation and conservation in soil, new aspects of (DHAR and MUKERJI) 155
  in the photo-oxidation of cane sugar (DHAR and MUKERJI 155
  in the induced and catalytic oxidation of glucose or cane sugar (DHAR and MUKERJI) 157
  in the oxidation of cane sugar mixed with soil and exposed to sunlight (DHAR and MUKHERJI) 159
  in the oxidation of molasses mixed with soil (DHAR and MUKHERJI) 161

Nitrogen in soil, a modified micro-method for the estimation of (SAHA) 72

O

PAGE

Optical activity and chemical constitution, studies on (SINGH and SINGH) 743
Organo-arsenic compounds, studies in (DAS-GUPTA) 305
Oxazole, acenaphthylene-ψ-phenyl-, acenaphthylene-, acenaphthylene-ψ -methyl- (SIRCAR and CHOWDHURY) 712
Oxidation with potassium iodate (SINGH and ILAHI) 717
Oxidation-reduction reaction, potentiometric studies in (SINGH and ILAHI) 717

P

Parachor and chemical constitution (RAY) 194
 of azoxybenzene, *p*-azoxyanisole, *p*-azoxyphenetole, *p*-methoxybenzalazine (RAY) 194, 195
 and the structure of formic acid (RAY) 484
Peptisation of a precipitate and its electrokinetic potential, on the relation between (CHAUDHURY and SENGUPTA) ... 670
Peroxidases, a potentiometric method of estimating their activity (DEY, RENGACHARI and SITHARAMAN) 390
Persulphate, estimation of (BANERJEE) 303
Phenacetin, preparation of compounds related to (KATRAK) ... 334
Phenanthrene from 9-hydroxyphenanthrene (CHATTERJEE) ... 659
Phenazoxine, hydroxy, acetnaphthahydroxy-,—acenaphtha-5-nitro-, and derivatives (SIRCAR and CHOWDHURY) 711, 712
Phenetole, β-hydroxy-*p*-nitro-, β-benzoyloxy-*p*-nitro-, β-salicyloxy-*p*-nitro-, β-chloro-*p*-nitro-, β-hydroxy-*p*-acetylamino-, β-hydroxy-*o*-nitro-, β-benzoyloxy-*o*-nitro-, β-hydroxy-*m*-nitro- (KATRAK) 335-336
Phenol, 4-chloro-2-methyl-, 2-chloro-4-methyl, 4-chloro-3-methyl-4-nitro-2-methyl-, 2-nitro-3-methyl-, synthesis of coumarins and chromones from (CHAKRAVARTI and BANERJEE) ... 622
Phenylacetic acid, 4-methoxy-5-carboxy- (SHAH and ALIMCHANDANI) 477
Phenyl (2:4-dimethoxy-) acetonitrile (MITTER and MAITRA) ... 238

PAGE

Phenyldihydroresorcinol, salical-bis-, benzal-bis-, cinnamal-bis-, furfural-bis-, *p*-dimethylaminobenzal-bis-, 3:4-methylenedioxybenzal-bis-, 4-hydroxy-3-methoxybenzal-bis, *o*-nitrobenzal-bis-, and derivativies (DESAI and WALI) ... 736-739

m (or *p*)-Phenylenediamine, *p*-toluene sulphonyl benzyl-(MENON and PEACOCK) 106, 107

Phenylethylamine, β-3:4-dimethoxy- (CHOPRA and RÂY) ... 479

Phthalic anhydride, (3-and 4-nitro-), condensation of, with phenol and anisole (MITTER and DUTT) 228

Phthalide (3:4:5-trimethoxy-) -carboxylic acid (CHOPRA and RÂY) 479

Phthalide, 3:4:5-trimethoxy-2-chloromethyl, 3:4:5-trimethoxy-2-cyanomethyl-, 3:4-methylenedioxy-5-methoxy-2-chloromethyl-, cyanomethyl- (PAUL) 600-601

Phthalide, 5:6-dimethoxy-2-(2′-hydroxy-3′-carboxy-5′-bromophenyl- and carbomethoxy derivative (MITTER and SEN-GUPTA) 449

Piperonyl, (6-nitro or 6-amino-) amide (BEDI and NARANG) ... 253

Polyhalides of ammonium and substituted ammonium bases (RAY and BHATTACHARYA) 456

Polyhalides, on the study of (RAY and BHATTACHARYA) ... 456

Propane, αβ-di (β′-trichloro -or tribormo-α′-hydroxyethoxy)-γ-hydroxy-, -αβ-(β′-trichloroethylidenedioxy)-γ-chloro-, and derivatives (MELDRUM and VAD) 119-120

*cyclo*Propane-1:2-dicarboxylic acid, *cis* and *trans-dl*-1-*iso*propyl, a synthesis of (RANGANATHAN) 419

Propionamide, β-dichlorovinyl-, chloral- (MELDRUM and BHOJRAJ) 186

Pyknometer, immersion (JUNG) 136

Pyrazole, 1-phenyl-3-(4′-chloro or bromo-1′-oxy)-β-naphthyl- (CHAKRAVARTI and BAGCHI) 694, 696

Pyrazole, 3:4:5-trimethyl-, 3:5-dimethyl-4-ethyl-, 3:5-phenylmethyl-3:4-dimethyl-, 3-phenyl-5-methyl-, 3-phenyl-4-methyl-, and derivatives (DE and RAKSHIT) 515

Pyrazole, (3-phenyl- 4:5-dimethyl-)-1-carbamidine nitrate (DE and RAKSHIT) 515

Pyrazole (5-phenyl-3-methyl-) carboxylic acid and derivatives (DE and RAKSHIT) 514

Pyrazolone, 3-methyl-, 3-phenyl-, and derivatives (DE and RAKSHIT) 517-518

PAGE

Pyrazolone, 2-carboxyimino-4-acetylphenylhydrazone-1-phenyl-, 3-carboxyimino-4-carbethoxy-, 3-carboxyimino-, 3-carboxyimino-4-benzylidene- (GHOSH) 90-91

Pyrazolone- (3-methyl-)-4-acetic acid and derivatives (DE and RAKSHIT) 514

Pyrazolone, 3-methyl-, 3:4-dimethyl-, 3-methyl-4-ethyl, 3:4:4-trimethyl-, 3-methyl-4-propyl-, 3-phenyl-and their 1-carbamidine nitrates (DE and RAKSHIT) 513

Pyruvic acid, 2:4-dimethoxyphenyl- (MITTER and MAITRA) ... 238

Q

Quinazolines (BEDI and NARANG) 253

Quinoline (2-*p*-anisyl-)-4-carboxylic-3-acetic acid (BOSE and GUHA) 703

Quinoline derivatives (NARANG, RAY and SACHDEVA) ... 260

R

Raman effect and molecular structure (GUPTA) 575

Red radish, experiments with (DEY, RENGACHARI and SITHARAMAN) 398

Resorcinol, 4:6-diethyl-2-methyl-, 4-ethyl-5-methyl-, 6-acetoxymercuri-, 4-ethyl-5:6 dimethyl-, 4:6-diethyl-5-methyl-, 4:6-diethyl-2:5-dimethyl- (SHAH and MEHTA) ... 361-367

Rice, effects of humidity and high temperature, on the NH_2 content of (BASU) 255

Ring glycerides, attempts to prepare (GOSWAMI and SHAHA) ... 464

S

Salicylic acid, chloral derivatives of (SHAH and ALIMCHANDANI) 475

Schardinger enzyme, identity with xanthine oxidase (BASU and MUKHERJEE) 11

Selenites, complex metal ammonium (RÂY and GHOSH) ... 494

Selenito-metalammines (complex) (RAY and GHOSH) ... 494

Silica, the physico-chemical properties of electro-dialysed gels of (BHATTACHARYA and GANGULI) 204, 547

Snake-venom, enzymes in (GHOSH and DE) 627

(GHOSH) 450

PAGE

Soils (alkali), molasses in the reclamation of (DHAR and MUKERJI) 175
Solanum xanthocarpum, Schard and Wendle, the chemical examination of (GUPTA and DUTT) 613
Spiro-compounds, a new route to (CHATTERJEE) 536
Stannic hydroxide sols, preparation and properties of (DHAR and VARADANAM) 602
Sulphur dichloride, interaction with substances containing the reactive methylene group (NAIK and VAISHNAV) ... 25

T

Tetrachloro-ββ-diglycerocitraconin, malein, palmitin, succinin (GOSWAMI and SHAHA) 465, 466
Tetrahydroquinoline sulphonic acids (acetyl), oxidation of (BOKIL) 404
Thioacetylcarbamic acid derivatives, formation of heterocyclic compounds from (Ghosh) 86
Thiocamphor, benzylidene-, *p*-methoxybenzylidene-, *p*-dimethylaminobenzylidene-, and derivatives (SEN) 524-525
    tautomeric behaviour of (SEN) 523
Thio*cylo*hexanone and derivatives (SEN) 270
Thio*cylo*pentanone and derivatives (SEN) 271
Thioketones (cyclic), studies on (SEN) 268
Thorium phosphate gel-forming mixtures during gelation, viscosity of (MEHTA, and PRASAD PARMAR) 128
Trichloromethylparaconic acid, constitution of the reduction product of (MELDRUM and KOTWAL) 213
3:4:5-Trimethoxy-2-phenylacetic acid (PAUL) 600
Trivalent nitrogen compounds, the stereochemistry of (MENON and PEACOCK) 104

V

n-Valeramide, chloral-, β-dichlorovinyl- (MELDRUM and BHOJRAJ) 186
Vanadous sulphate, use as a reducing agent (BANERJEE) ... 301

PAGE

Viscosity and transparency, as general criteria of coagulation, inadmissibility of (JOSHI and PANIKKAR) 439
Vitamin C, studies in (RUDRA) 740
Vitex negundo, constituents of the leaves of (GHOSE and KRISHNA) 634

X

Xanthine oxidase, identity with Schardinger enzyme (BASU and MUKHERJEE) 11

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